



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification 5 :</b> <b>C08G 61/02, 61/12, H01B 1/12</b> <b>H05B 33/14</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 92/03490</b> <b>(43) International Publication Date:</b> <b>5 March 1992 (05.03.92)</b>
<b>(21) International Application Number:</b> PCT/GB91/01420 <b>(22) International Filing Date:</b> 22 August 1991 (22.08.91) <b>(30) Priority data:</b> 9018698.2                      24 August 1990 (24.08.90)                      GB <b>(71) Applicants:</b> CAMBRIDGE RESEARCH AND INNOVATION LIMITED [GB/GB]; CAMBRIDGE CAPITAL MANAGEMENT LIMITED [GB/GB]; 13 Station Road, Cambridge CB1 2JB (GB). LYNXVALE LIMITED [GB/GB]; The Old Schools, Trinity Lane, Cambridge CB2 1TS (GB). <b>(72) Inventors:</b> HOLMES, Andrew ; 19 Newton Road, Cambridge, CB2 2AL (GB). BRADLEY, Donal, Donat, Con- or ; 48 Cambridge Road, New Wimpole, Cambridge SG8 5QE (GB). KRAFT, Arno ; 3 Pemberton Terrace, Cambridge CB2 1JA (GB). BURN, Paul ; Christs College, Cambridge (GB). BROWN, Adam ; Whitfield House, 69 Grange Road, Cambridge CB3 9AA (GB). FRIEND, Richard ; 6 Sherlock Road, Cambridge CB3 0HR (GB).		<b>(74) Agents:</b> DRIVER, Virginia, R. et al.; Page White & Farrer, 54 Doughty Street, London WC1N 2LS (GB). <b>(81) Designated States:</b> AT (European patent), AU, BE (European patent), BR, CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FI, FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, KR, LU (European patent), NL (European patent), SE (European patent), SU+.
<b>(54) Title:</b> SEMICONDUCTIVE COPOLYMERS FOR USE IN LUMINESCENT DEVICES  <b>(57) Abstract</b> <p>A semiconductive conjugated copolymer comprises at least two chemically different monomer units which, when existing in their individual homopolymer forms, have different semiconductor bandgaps. The proportion of said at least two chemically different monomer units in the copolymer is selected to control the semiconductor bandgap of the copolymer so as to control the optical properties of the copolymer. The copolymer is formed in a manner enabling it to be laid down as a film without substantially affecting the luminescent characteristics of the copolymer and is stable at operational temperature. The semiconductor bandgap may be spatially modulated so as to increase the quantum efficiency of the copolymer when excited to luminescence, to select the wavelength of radiation emitted during luminescence or to select the refractive index of the copolymer.</p>		

# + DESIGNATIONS OF "SU"

Any designation of "SU" has effect in the Russian Federation. It is not yet known whether any such designation has effect in other States of the former Soviet Union.

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TITLE OF THE INVENTIONSEMICONDUCTIVE COPOLYMERS FOR USE IN LUMINESCENT DEVICESFIELD OF THE INVENTION

This invention relates to semiconductive copolymers for use in luminescent devices, particularly electroluminescent devices.

BACKGROUND TO THE INVENTION

It has been shown that certain conjugated polymers show a relatively high quantum efficiency for the radiative decay of singlet excitons. Of these, poly-p-phenylene vinylene (PPV) can be prepared via a solution-processible precursor polymer, and although itself intractable and not easily processed, can be prepared in the form of thin films of high quality by thermal conversion of the as-prepared films of the precursor polymer. Details of this general synthesis method are given in "Precursor route poly(p-phenylene vinylene): polymer characterisation and control of electronic properties", D.D.C. Bradley, J. Phys. D: Applied Phys. 20, 1389 (1987), and "Spectroscopic and cyclic voltammetric studies of poly(p-phenylene vinylene) prepared from two different sulphonium salt precursor polymers", J.D. Stenger-Smith, R.W. Lenz and G. Wegner, Polymer 30, 1048 (1989). Measurements of photoluminescence, PL, have been reported by for example "Optical Investigations of Conjugated Polymers", R.H. Friend, J. Molecular Electronics, 4, 37 (1988), and "Photoexcitation in Conjugated Polymers", R.H. Friend, D.D.C. Bradley and P.D. Townsend, J. Phys. D 20, 1367 (1987). In our earlier International Patent Application No. PCT/GB90/00584 (Publication No. PCT/WO90/13148) films of PPV are disclosed as being useful as the emissive layer in a structure exhibiting electroluminescence (EL). This structure requires injection of electrons and holes from either side of the active (i.e.

emissive) region of the film, and various metallic contact layers can be used. In sandwich-like structures, and for emission from the plane of the device, one of these should be semi-transparent.

The advantages of using polymers of this type as the emissive layer in EL structures include:

- (a) ease of fabrication of large area structures. Various methods are available for solution-processing of the precursor polymer, including spin-coating from solution which is the preferred method, and dip-coating;
- (b) intractability of the polymer film, giving desirable strength, resistance to degradation from heat and exposure to oxygen, resistance to structural changes such as recrystallisation and shrinkage, and resistance to ion migration;
- (c) intrinsically good properties for luminescence, including low densities of charges and/or spin-carrying defects.

However, there is some evidence that the quantum yield for radiative decay of the excited states is lowered through their migration to non-radiative decay centres, see for example "Radiative and Non-Radiative Recombination Processes in Photoexcited Poly(p-phenylenevinylene)", D.D.C. Bradley, R.H. Friend, K.S. Wong, W. Hayes, H. Lindenberger and S. Roth, Springer Solid State Sciences, 76, 107 (1987), and "Light-Induced Luminescence Quenching in Precursor-Route Poly(p-phenylenevinylene)" D.D.C. Bradley and R.H. Friend, J. Phys. CM 1, 3671 (1989).

SUMMARY OF THE INVENTION

The present invention is directed to providing polymers for use as the emissive layer in EL structures which overcome these difficulties.

According to one aspect of the present invention there is provided a semiconductive conjugated copolymer comprising at least two chemically different monomer units which, when existing in their individual homopolymer forms, have different semiconductor bandgaps, the proportion of said at least two chemically different monomer units in the copolymer having been selected to control the semiconductor bandgap of the copolymer so as to control the optical properties of the copolymer, said copolymer having been formed in a manner enabling it to be laid down as a film without substantially affecting the luminescent characteristics of the copolymer, said copolymer being stable at operational temperature.

The operational temperature depends upon the use to which the copolymer is put. Typically, use of the copolymer in luminescence devices may require the operational temperature to be ambient temperature or room temperature. Preferably, the stability of the copolymer extends to operational temperatures in the range 0 - 150 °C, more preferably down to 77°K. Preferably the monomer units in the copolymer are arylene vinylene units.

A semiconductor is a material that is able to accommodate charged excitations which are able to move through this material in response to an applied electrical field. Charge excitations are stored in the semiconductor in states which are (or are derived from) conduction band states (in the language of quantum chemistry, lowest unoccupied molecular orbitals, LUMOs) if negatively charged, or valence band states (highest occupied molecular orbitals, HOMOs) if positively charged. The semiconductor band gap is the energy difference between valence and conduction bands (or from HOMO to LUMO)

The present application is primarily concerned with copolymers in which the material is made up of chemically distinct regions of polymer chain. A convenient description of the electronic states (molecular orbitals) is one in which the wavefunctions are substantially localised on a region of chain of one chemical type. It is useful to define the semiconductor bandgap locally, i.e. as the energy gap between HOMO and LUMO on a particular sequence of polymer chain to which the HOMO and LUMO wavefunctions are substantially confined. One can expect to find a variation of gap from HOMO to LUMO between regions of one chemical type those of another. This may be described as a spatial modulation of the bandgap.

The inventors have found that by modulating the semiconductor bandgap of the copolymer it is possible to increase the quantum efficiency of the copolymer when excited to luminesce. Quantum efficiency for luminescence may be defined as photons out per excited state. For photoluminescence this is identified as photons out per photon absorbed. For electroluminescence this is defined as photons out per electron injected into the structure.

They have also found that the semiconductor bandgap can be modulated to control the wavelength of radiation emitted during luminescence. This gives the very desirable feature of controlling the colour of light output from the polymer. The inventors have also found that the semiconductor bandgap is a factor affecting the refractive index of the copolymer.

In one aspect, the chain of the copolymer is fully conjugated. In a further aspect, at least one of the monomer units is not fully conjugated in the chain of the copolymer. It will be apparent that it is an important feature of the invention that the copolymer, when laid down as a film, comprises two chemically different monomer units. This can be achieved by converting a suitable precursor copolymer

comprising a selected proportion of the different monomer units or by controlling the extent of conversion of a precursor polymer into a conjugated copolymer. The conjugated polymers used here are all examples of semiconductors, and there is some control of bandgap through adjustment of the repeat units of the chain. However, it is also found that it is useful to incorporate some units of non-conjugated polymers to form some of the copolymers. In this case, the non-conjugated section of the chain would function as a very large gap semiconductor, so that under the conditions of operation found here it would behave as an insulator, i.e. there would be little or no charge storage on or movement through such a region of the chain. In this case, the material as a whole will still function as a semiconductor so long as there is a path through the bulk of the sample that passes entirely through the semiconducting regions of the chain (those that are conjugated). The threshold for the existence of such a path is termed the percolation threshold, and is usually found to be in the region of 20% volume fraction of non-insulating material. In the present specification, all such copolymers are well above this percolation threshold and can be termed as semiconductors.

In a preferred embodiment the present invention provides a conjugated poly(arylene vinylene) copolymer capable of being formed as a thin electroluminescent film, wherein a proportion of the vinylic groups of the copolymer are saturated by inclusion of a modifier group substantially stable to elimination during formation of the film, whereby the proportion of saturated vinylic groups controls the extent of conjugation, thereby modulating the semiconductor ( $\pi - \pi^*$ ) bandgap of the copolymer.

In another aspect, the invention provides a method of manufacturing a semiconductive copolymer comprising:

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(a) reacting a quantity of a first monomer with a quantity of a second monomer in a solvent comprising a mixture of water and an alcohol;

(b) separating the reaction product therefrom;

(c) dissolving the reaction product in an alcohol the same as or different from said first mentioned alcohol;

(d) forming from the result of step (c) a conjugated polymer film the quantities in step (a) being selected so that in the conjugated polymer the semiconductor bandgap is controlled so as to control the optical properties of the copolymer.

Step (a) is preferably carried out in the presence of a base.

The present invention also provides a method of forming a conjugated poly(arylene vinylene) copolymer as defined above, which method comprises heating substantially in the absence of oxygen a poly(arylene-1,2-ethanediyl) precursor copolymer wherein a proportion of the ethane groups include a modifier group substituent and at least some of the remaining ethane groups include a leaving group substituent, whereby elimination of the leaving group substituents occurs substantially without elimination of the modifier group substituents so as to form the conjugated poly(arylene vinylene) copolymer.

The extent of conjugation of the conjugated poly(arylene vinylene) copolymer can be tailored by appropriate selection of the arylene constituents of the copolymer and of the modifier group. For example, phenylene moieties incorporating electron-donating substituent groups or arylene moieties with oxidation potentials lower in energy than that of phenylene are found to incorporate the modifier group preferentially as



compared with the corresponding unsubstituted arylene moiety. Thus, the proportion of vinylic groups saturated by incorporation of the modifier group can be controlled by selection of the arylene moieties' substituents and the extent of conjugation of the copolymer may be concomitantly modulated. The extent of conjugation of the copolymer affects the  $\pi - \pi^*$  bandgap of the copolymer. Therefore, selection of appropriate reaction components may be used to modulate the bandgap. This property may be exploited, for example, in the construction of electroluminescent devices as described in more detail with reference to the preferred embodiment.

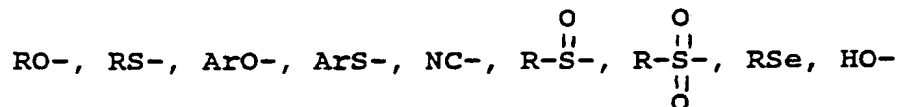
In a further aspect, the present invention also provides a poly(arylene-1,2-ethanediyl) precursor copolymer wherein a proportion of the ethane groups include a modifier group substituent and at least some of the remaining ethane groups include a leaving group substituent, the precursor copolymer being convertible by elimination of the leaving group substituents into a conjugated poly(arylene vinylene) copolymer as defined above.

The invention also provides a method of conversion of the precursor into its copolymer in which the extent of elimination of the leaving group constituents is controlled to control the bandgap of the copolymer to define both the colour of luminescence of the resulting copolymer film and its quantum efficiency for luminescence.

In a further aspect, there is provided a method of forming a poly(arylene-1,2-ethanediyl) precursor copolymer as defined above, which method comprises reacting a first monomer component with a second monomer component, in the presence of base and a solvent comprising a modifier group, wherein the first monomer component comprises a first arylene moiety substituted with  $-\text{CH}_2\text{L}^1$  and  $-\text{CH}_2\text{L}^2$  and the second monomer component comprises a second arylene moiety substituted with  $-\text{CH}_2\text{L}^3$  and  $-\text{CH}_2\text{L}^4$ , in which  $\text{L}^1$ ,  $\text{L}^2$ ,  $\text{L}^3$  and  $\text{L}^4$  each represents a leaving group

substituent which may be the same or different from one another. This method may constitute a first step in the formation of the conjugated poly(arylene vinylene) copolymer.

A function of the modifier group is to interrupt the conjugation of the poly(arylene vinylene) copolymer by saturation of the vinylic groups of the copolymer chain. Thus, for the modifier group to be successful in this function it must be relatively stable to elimination during formation of the poly(arylene vinylene) copolymer. Typical modifier groups include:



A preferred modifier group is a C<sub>1</sub> to C<sub>6</sub> alkoxy group, more preferably a methoxy group.

The poly(arylene-1,2-ethanediyl) precursor copolymer may be formed in a first step by reacting a first monomer component with a second monomer component, in the presence of base and a solvent comprising the modifier group, wherein the first monomer component comprises a first arylene moiety substituted with -CH<sub>2</sub>L<sup>1</sup> and -CH<sub>2</sub>L<sup>2</sup> and the second monomer component comprises a second arylene moiety substituted with -CH<sub>2</sub>L<sup>3</sup> and -CH<sub>2</sub>L<sup>4</sup>, in which L<sup>1</sup>, L<sup>2</sup>, L<sup>3</sup> and L<sup>4</sup> each represents a leaving group substituent which may be the same or different from one another.

In the step of forming the poly(arylene-1,2-ethanediyl) precursor copolymer the solvent preferably also includes water. Thus, for aqueous solvents, the modifier group must be present as a water miscible polar solvent/reagent. Where the modifier group is alkoxy, the corresponding solvent or solvent

component would therefore be an alcohol. Preferably the solvent comprises at least 30% modifier group by weight. More preferably the solvent is water: methanol at a ratio of 1:1 or lower. Modifier groups may be introduced selectively either during formation of the precursor copolymer or by displacement reactions on the precursor copolymer.

The identity of the leaving groups is not particularly critical provided that the first and second monomer components may react together in the presence of base and provided that the leaving group substituents on the poly(arylene-1,2-ethanediyl) precursor copolymer may eliminate upon heating. Typical leaving groups include 'onium salts in general, bearing a non-basic counter anion. Sulphonium salts, halides, sulphonates, phosphates or esters are suitable examples of leaving groups. Preferably a sulphonium salt such as a tetrahydrothiophenium salt is used.

Throughout this specification the term arylene is intended to include in its scope all types of arylenes including heteroarylenes as well as arylenes incorporating more than one ring structure, including fused ring structures.

At least two arylene moieties are present in the copolymer chain and these may be substituted or unsubstituted arylene or heteroarylene moieties. Suitable substituents include alkyl, O-alkyl, S-alkyl, O-aryl, S-aryl, halogen, alkyl sulphonyl and aryl sulphonyl. Preferred substituents include methyl, methoxy, methyl sulphonyl and bromo, and the arylenes may be substituted symmetrically. In a more preferred embodiment of the invention, one of the arylene moieties of the copolymer is unsubstituted and comprises para-phenylene. Preferably, the second component is selected from the group comprising 2,5-dimethoxy-para-phenylene, 2,5-thienylene, 2,5-dimethyl-para-phenylene, 2-methoxy-5-(2'methylpentyloxy)-para-phenylene and 2-methoxy-5-(2'ethylhexyloxy)-para-phenylene. More preferably

the para-phenylene moiety is present in the copolymer chain in an amount resulting from conversion of a precursor copolymer formed by reaction of at least 70 mole % of the PPV precursor monomer unit.

Referring in particular to the method of forming the conjugated polyarylene vinylene copolymer, this can be effected by heating, preferably in a temperature range of 70-300°C. The heating is performed substantially in the absence of oxygen, for example under an inert atmosphere such as that of one or more inert gases or under vacuum.

In the step of forming the precursor copolymer, a range of reaction temperatures and reaction times is possible. The reaction temperature is constrained mainly by the temperature range at which the solvent is liquid and typically varies from -30°C to +70°C, preferably -30°C to +30°C, more preferably -5°C to +10°C. The reaction time may typically be between 1 minute and 1 day, depending on the temperature and reaction components, preferably not greater than 4 hours. Once the precursor copolymer is formed this may optionally be purified, for example by precipitation with a salt of a non-nucleophilic counter anion (i.e. anion exchange). Preferably the precursor copolymer is dialysed against an appropriate solvent such as water or a water-alcohol mixture. Choice of the base used in the reaction is not particularly critical provided that it is soluble in the solvent. Typical bases include hydroxides or alkoxide derivatives of Group I/II metals and may be present at a ratio of 0.7-1.3 mole equivalents of base per mole of monomer. Preferably, hydroxides of lithium, sodium or potassium are used in equimolar proportions with the monomer.

In a further embodiment, at least one of the monomer units of the copolymer comprises an arylene vinylene unit substituted with a solubilizing group in the arylene ring so as to render

the copolymer soluble. Any known solubilizing group may be used for this purpose. Where the copolymer is to be soluble in water, a charged solubilizing group is preferred. The solubilizing group typically comprises an alkoxy group of at least 4 carbon atoms. The alkoxy group may be branched or linear and preferably introduces asymmetry into the arylene rings so as to disrupt the packing of the copolymer chains. Preferably the alkoxy group is a 2-methylpentyloxy or a 2-ethylhexyloxy group. A further alkoxy group such as a methoxy group may be substituted para to the solubilizing group.

By making the copolymer soluble, this confers the advantage of allowing the copolymer to be processed in solution. Accordingly, a solution-processable conjugated copolymer may be provided in which the monomer units have been selected to modulate the semiconductor bandgap thereof. In this way, the quantum efficiency of the copolymer can be increased and the wavelength of radiation emitted during luminescence can be selected.

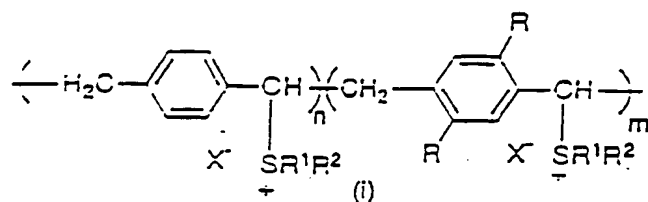
In a further aspect, the present invention also provides a method of forming a conjugated poly(arylene vinylene) copolymer. The method comprises heating substantially in the absence of oxygen a poly(arylene-1,2-ethanediyl) precursor polymer wherein at least some of the ethane groups include a modifier group substituent, the heating conditions being controlled so that elimination of the modifier group substituents occurs to form the copolymer whereby a proportion of the vinylic groups of the copolymer remain saturated by the modifier group substituents, the proportion of saturated vinylic groups controlling the extent of conjugation in the copolymer, thereby modulating the semiconductor bandgap of the copolymer.

In this aspect of the invention, the precursor polymer is formed whereby substantially all the leaving groups are replaced by the modifier groups. A suitable method for forming the precursor polymer is to be found in Tokito et al Polymer (1990), vol. 31, p.1137. By replacing the leaving group with a modifier group which is substantially stable at ambient temperatures, a relatively robust precursor polymer is formed. Examples of typical modifier groups are set out in the foregoing discussion. Advantageously the modifier group is an alkoxy group, preferably a methoxy group.

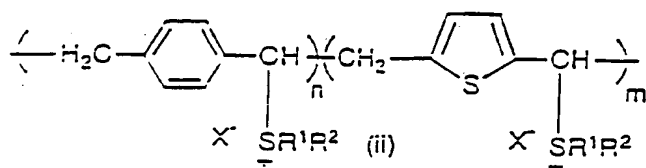
Advantageously the precursor polymer comprises a homopolymer, preferably a poly(paraphenylene-1,2-ethanediyl) polymer, a poly(2,5 dimethoxy para phenylene-1,2-ethanediyl) polymer, or a poly(thienylene-1,2-ethanediyl) polymer. Partial elimination of the modifier groups from the homopolymer produces a copolymer.

By controlling the extent of conversion to the copolymer, the extent of conjugation in the copolymer is controlled. This therefore provides a further route for modulating the semiconductor bandgap of the copolymer. The heating of the precursor polymer is preferably performed substantially in the absence of acid. The presence of acid tends to result in conversion to the fully conjugated polymer. By controlling the temperature of heating and the time of heating it is possible to control the degree of conversion into the copolymer, thereby modulating the semiconductor bandgap of the copolymer. Thus, the wavelength of radiation emitted during luminescence of the materials may be selected by controlling the heating conditions. The more conversion to the conjugated copolymer, the more red-shifted the wavelength becomes. In this way, it is possible to control the colour of the emissions from blue to red. Preferably, the temperature of heating is in the range 200 - 300°C and preferably the heating time is up to 12 hours.

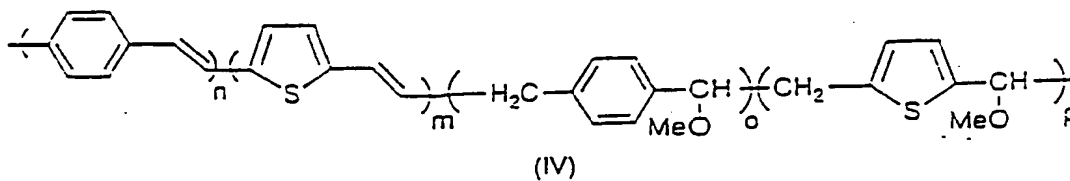
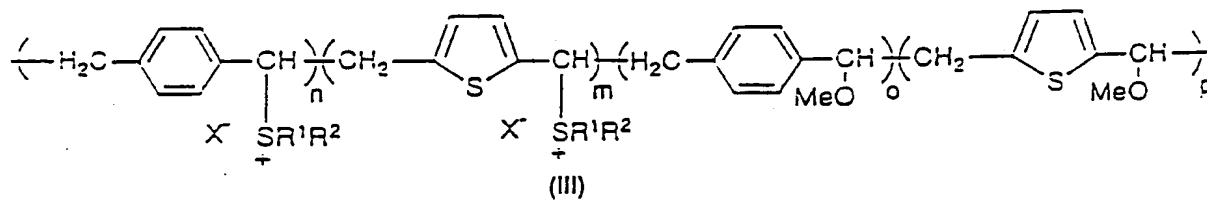
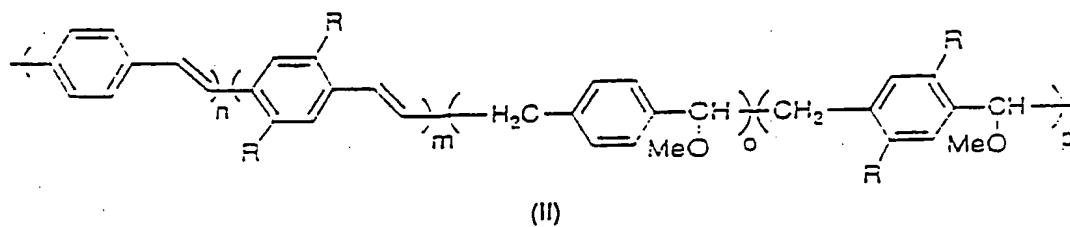
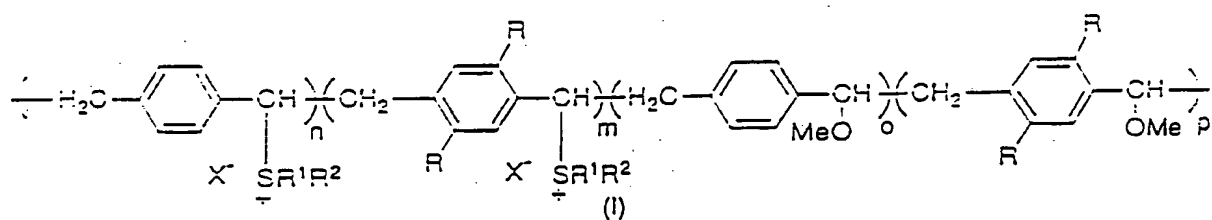
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R = OMe

R<sup>1</sup>, R<sup>2</sup> =  $-(\text{CH}_2)_4-$  or  $\text{CH}_3-$ 

R = H or OMe

R<sup>1</sup>, R<sup>2</sup> =  $-(\text{CH}_2)_4-$  or  $\text{CH}_3-$ 

Referring to the foregoing page of structural formulae, copolymers of type (i) have been prepared by Lenz et al from the tetrahydrothiophenium salts of the two monomer units as described in "Highly conducting, iodine-doped copoly(phenylene vinylene)s", C.-C. Han, R.W. Lenz and F.E. Karasz, Polym. Commun. 28, 261 (1987) and "Highly conducting, iodine-doped arylene vinylene copolymers with dialkoxyphenylene units", R.W. Lenz, C.-C. Han and M. Lux, Polymer 30, 1041 (1989). Copolymers of type (ii) have been prepared by Lenz et al from the tetrahydrothiophenium salts of the two monomer units as described in "Synthesis and electrical conductivity of poly(1,4-phenylenevinylene-co-2,5-thienylenevinylene)", H.-K. Shim, R.W. Lenz and J.-I. Hin, Makromol. Chem 190, 389 (1989) and have been mentioned by K.Y.A. Jen, R.L. Elsenbaumer, L.W. Shacklette (Allied Corp.), PCT Int. Appl. Pub. No. WO 8800954. These copolymers were produced as intermediate products to the final products prepared by Lenz, these final products being heavily doped with strong oxidants to enable conductivity measurements to be undertaken. The intermediate products were not of interest themselves.

Furthermore, they were prepared under aqueous reaction conditions. Direct comparison of the materials prepared in Lenz et al and the materials prepared by the method of the preferred embodiments of the present invention showed that they were different for a number of reasons.



First, the use of water/alcohol mixtures as a solvent allows better control over the relative proportions of fragments of each monomer observed in the final co-polymers. This is observed by IR spectroscopy and micro-analysis.

Second, the use of water/alcohol in the present process allows selective substitution of the sulphonium leaving group with the alcohol. This occurs at a faster rate at benzylic carbons which are attached to an activated phenylene ring, for example, a dimethoxy substituted phenylene ring. This option is not open to the Lenz process. Evidence for substitution comes from nuclear magnetic resonance (NMR), infrared (IR), and photoluminescence studies and also from reactions observed on the homopolymers. For example, dimethoxy-PPV is prepared from a precursor polymer which has methoxy modifier groups. This polymer is in turn prepared according to the literature (T. Momii, S. Tokito, T. Tsutsui and S. Saito - Chem. Letters (1988), 1201) from the precursor polymer which has sulphonium leaving groups by exchanging the chloride anion with a p-toluenesulphonate anion and then reacting this material with methanol. It has been observed by the inventors that it is not necessary to exchange anions for the substitution reaction to occur in the dimethoxy-PPV precursor polymer. It has also been found by the inventors that the reaction of the sulphonium precursor polymer of PPV with methanol occurs at a much slower rate. The precursor co-polymers prepared by the method of the preferred embodiments of the present invention can therefore be better described by the structures of General Formulae (I) and (III).

Third, the usual method of conversion of precursor polymers with methoxy modifier groups is by heating under acidic conditions. With the method of the present invention it is preferred to use heat treatment alone as this allows the methoxy modifier groups to remain in part uneliminated thus

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segregating the conjugated material into discrete segments as described by General Formulae II and IV. This solution and method represents a significant advancement over the art. Thin films prepared by this method are stable to the loss of the methoxy modifier groups (for example, thin films heated for 2 h had similar properties to thin films heated for 24 h). This is evidenced by IR and ultraviolet/visible (UV/vis) spectroscopy.

Fourth, the use of water/alcohol mixtures increases the reaction rate of both monomeric units compared with just using water as the solvent during polymerisation. This is evidenced by comparison of the amount of acid necessary to neutralise the remaining unreacted base in Example 1 and in the examples described by Lenz.

Finally, the quality of films cast from a methanol solution as opposed to an aqueous solution is far superior and easily reproducible, and gives higher light output in electroluminescent devices. The quality of films was determined by Dek Tak profilometry.

In the following when reference is made to ratios of PPV, dimethoxy-PPV, PTV, dimethyl-PPV 2-methoxy-5-(2'-methylpentyloxy)-PPV and 2-methoxy-5-(2'-ethylhexyloxy)-PPV monomer units in both precursor and conjugated copolymer structures the ratios are defined by the amounts of the corresponding monomer units used in the initial polymerisation reaction.

For a better understanding of the present invention and to show how the same may be carried into effect, reference will now be made by way of example to the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a diagram showing an example of the steps of a method for producing the copolymers prepared via a soluble precursor;

Figure 2a is a graph showing the absorption spectra of spin-coated thin films of PPV and copolymers of PPV, as the majority constituent, and dimethoxy-PPV (DMeOPPV) as converted at 220°C in vacuo for 2 hours

Curve a is PPV homopolymer

Curve b is 95% PPV to 5%DMeOPPV

Curve c is 90% PPV to 10% DMeOPPV

Curve d is 85% PPV to 15% DMeOPPV

Curve e is 80% PPV to 20% DMeOPPV

Curve f is 70% PPV to 30% DMeOPPV

Figure 2b is a graph showing the absorption spectrum of a spin-coated thin film of dimethoxy-PPV as converted at 220°C in the presence of acid for two hours.

Figures 3a and 3b are graphs showing respectively the emission spectra for thin spin coated and thick solution cast films of a copolymer produced from a 1:9 molar ratio of dimethoxy-PPV and PPV monomer units respectively, converted at 220°C in vacuo for two hours;

Figures 4a and 4b are graphs showing respectively the emission spectra for thin spin coated and thick solution cast films of a copolymer produced from a 1:4 molar ratio of dimethoxy PPV and PPV monomer units respectively, converted at 220°C in vacuo for two hours;

Figures 5a and 5b are graphs showing respectively the photoluminescence spectra for homopolymers of PPV and dimethoxy PPV;

Figures 6a, b and c are graphs showing respectively the absorption spectra of a homopolymer of PPV, and random copolymers of PPV and PTV produced respectively from 19:1 and 9:1 molar ratios of PPV and PTV monomer units, converted at 220°C in vacuo for two hours;

Figures 7a, b and c are graphs showing respectively the photoluminescence emission spectra for thick free cast films of a homopolymer of PPV; a copolymer produced from a 19:1 molar ratio of PPV and PTV monomer units respectively; and a copolymer produced from a 9:1 molar ratio of PPV and PTV monomer units respectively;

Figures 8a, b and c are graphs showing the absorption spectra of spin-coated thin films of a homopolymer of PPV, and random copolymers of PPV and dimethyl PPV produced respectively from 19:1 and 9:1 molar ratios of PPV and PTV dimethyl monomer units as converted at 220°C in vacuo for two hours;

Figures 9a, b and c are graphs showing respectively the photoluminescence emission spectra of thick free cast films for the homopolymer of PPV; a copolymer produced from a 19:1 molar ratio of PPV and dimethyl PPV monomer units respectively; and a copolymer produced from a 9:1 molar ratio of PPV and dimethyl-PPV monomer units respectively;

Figures 10a, 11a and 12a are graphs showing the current/voltage characteristics of a thin film of respectively PPV; a copolymer produced from a 9:1 molar ratio of PPV and dimethoxy PPV monomer units respectively; and a copolymer produced from a 9:1 molar ratio of PPV and thienylene vinylene monomer units respectively, the polymer films being spin-coated and converted at 220°C for two hours in vacuo with hole injecting electrodes of oxidised aluminium, and with electron injecting electrodes of aluminium;

Figures 10b, 11b and 12b are graphs showing the luminescence/current relationship for a thin film of respectively PPV; a copolymer produced from a 9:1 molar ratio of PPV and dimethoxy PPV monomer units respectively; and a copolymer produced from a 9:1 molar ratio of PPV and thienylene vinylene monomer units respectively, the polymer films being spin-coated and converted at 220°C for two hours in vacuo with hole injecting electrodes of oxidised aluminium, and with electron injecting electrodes of aluminium;

Figure 13 illustrates the electroluminescent quantum yield of random copolymers formed from PPV and dimethoxy-PPV monomer units as measured in thin film structures with hole injecting electrodes of oxidised aluminium, a spin-coated film converted at 220°C in vacuo for two hours, and with electron injecting electrodes of aluminium;

Figure 14 illustrates the electroluminescent quantum yield of random copolymers formed from PPV and PTV monomer units as measured in thin film structures with hole injecting electrodes of oxidised aluminium, a spin-coated film converted at 220°C in vacuo for two hours, and with electron injecting electrodes of aluminium;

Figure 15 illustrates the electroluminescent quantum yield of random copolymers formed from PPV and dimethyl-PPV monomer units as measured in thin film structures with hole injecting electrodes of oxidised aluminium, a spin-coated film converted at 220°C in vacuo for two hours, and with electron injecting electrodes of aluminium;

A film of copolymer of 10% DMeOPPV: 90% PPV was spin-coated and an area was capped with 500Å of evaporated aluminium. The sample was then thermally converted for 12 hours at 220°C in vacuo. The aluminium capping layer was

removed by reacting it in dilute alkali. Figures 16 and 17 show the optical absorption spectra and photoluminescent spectra for two areas in a polymer film which have undergone different conversion treatments;

Figures 18a, 18b, 18c are graphs showing the infrared spectra of precursor to random copolymers of PPV and MMP-PPV(2-methoxy-5-(2'-methylpentyloxy)-PPV produced from 80 : 20, 90 : 10, and 95 : 5 w/w ratios of PPV and MMP-PPV monomer units, respectively;

Figure 19a, 19b, 19c, 19d, are graphs showing the absorption spectra of spin-coated thin films of random copolymers of PPV and MMP-PPV produced from 80 : 20, 90 : 10, and 95 : 5 and 100 : 0 w/w ratios of PPV and MMP-PPV monomer units, respectively as converted at 220°C in vacuo for 12 hours;

Figure 20 is a graph showing the current/voltage characteristics of a thin film of a random copolymer of PPV and MMP-PPV produced from 90 : 10 w/w ratio of PPV and MMP-PPV monomer units as converted in vacuo at 220°C for 12 hours on a substrate of ITO-coated glass and with calcium as a cathode;

Figure 21 is a graph showing the luminance/current characteristics of a thin film of a random copolymer of PPV and MMP-PPV produced from 90 : 10 w/w ratio of PPV and MMP-PPV monomer units as converted in vacuo at 220°C for 12 hours on a substrate of ITO-coated glass and with calcium as a cathode;

Figures 22a and 22b are graphs showing the infrared spectra of precursors of random copolymers of PPV and MEH-PPV (2-methoxy-5-(2'-ethylhexyloxy)-PPV produced from 90 : 10 and 95 : 5 w/w ratios of PPV and MEH-PPV (2-methoxy-5-(2'-ethylhexyloxy)-PPV) monomer units respectively;

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Figures 23a, 23b, 23c, 23d are graphs showing the absorption spectra of spin-coated thin films of random copolymers of PPV and MEH-PPV produced from 80 : 20, 90 : 10, 95 : 5 and 100 : 0 w/w ratios of PPV and MEH-PPV monomer units, respectively as converted at 220°C in vacuo for 12 hours;

Figure 24 is a  $^1\text{H}$  NMR spectrum of the copolymer described in example 11 produced from 5 : 95 w/w ratio of PPV and MEH-PPV monomer units;

Figures 25a, 25b, 25c are graphs showing the infrared spectra of (c) MEH-PPV and of random copolymers of PPV and MEH-PPV produced from (a) 20 : 80 and (b) 5 : 95 w/w ratios of PPV and MEH-PPV monomer units, respectively, by the method described in example 11;

Figure 26 is a graph showing the absorption spectra of spin-coated thin films of MEH-PPV and of random copolymers of PPV and MEH-PPV produced from 20 : 80 and 5 : 95 w/w ratios of PPV and MEH-PPV monomer units, respectively;

Figures 27a and 27b are graphs showing the photoluminescence emission spectra of random copolymers of PPV and MEH-PPV produced from 20 : 80 and 5 : 95 w/w ratios of PPV and MEH-PPV monomer units, respectively;

Figures 28a and 28b are graphs showing the electroluminescence spectra for random copolymers of PPV and MEH-PPV produced from 20 : 80 and 5 : 95 w/w ratios of PPV and MEH-PPV monomer units, respectively;

Figures 29a and 29b are graphs showing the current/voltage characteristics and luminance/voltage relationship for a thin film of a random copolymer of PPV and MEH-PPV produced from 20 : 80 w/w ratio of PPV and MEH-PPV monomer units thin; films were spin-coated onto substrates of ITO coated glass and aluminium cathodes were evaporated on top;

Figures 30a and 30b are graphs showing the current/voltage characteristics and luminance/voltage relationship for a thin film of random copolymer of PPV and MEH-PPV produced from 5 : 95 w/w ratio of PPV and MEH-PPV monomer units: thin films were spin-coated onto substrates of ITO coated glass and aluminium cathodes were evaporated on top;

Figure 31 is a scatter graph showing the quantum yield of random copolymers formed from PPV and MMP-PPV monomer units as measured in thin film structures with hole injecting electrodes of oxidised aluminium, a spin-coated film converted at 220°C in vacuo for 12 hours, and with electron injecting electrodes of aluminium;

Figure 31a is a graph showing the photoluminescence spectra of MEH-PPV and random copolymers of (a) MEH-PPV and PPV produced from (b) 95 : 5 and (c) 80 : 20 w/w ratios of MEH-PPV and PPV monomer units, respectively;

Figures 32 (a to d) show respectively the formal structural formulae of: the THT-leaving PPV precursor; the MeO-leaving PPV precursor; PPV; and partially converted MeO-leaving PPV;

Figure 33 is a graph showing the absorption spectra of precursors of THT-leaving PPV (broken) and MeO-leaving PPV (solid);

Figure 34 is a graph showing the absorption spectra of THT-leaving PPV (broken) and MeO-leaving PPV (solid) after thermal conversion at 300°C for 12 hours in vacuo;

Figure 35 is a graph showing the absorption spectra of thin spin-coated films of MeO-leaving PPV before (dotted) and after (solid) thermal conversion at 300°C for 12 hours in vacuo;



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Figures 36 (a) and (b) are graphs showing respectively the current-voltage and luminance-current characteristics of THT-leaving PPV as converted in vacuo at 220° for 12 hours on a substrate of ITO-coated glass and with aluminium as a cathode;

Figures 37 (a) and (b) are graphs showing respectively the current-voltage and luminance-current characteristics of MeO-leaving PPV as converted in vacuo at 300° for 12 hours on a substrate of ITO-coated glass and with aluminium as a cathode;

Figure 38 is a graph showing the electroluminescence emission spectra of THT-leaving PPV (dotted) and MeO-leaving PPV (solid) after thermal conversion;

Figures 39(a) to (c) show respectively the formal structural formulae of the random copolymers of: PPV and DMeOPPV in precursor form; as converted thermally in vacuo; and as converted thermally in the presence of acid;

Figure 40 is a graph showing the absorption spectra of spin-coated thin films of random copolymers of PPV and DMeOPPV after thermal conversion as converted in vacuo at 220°C for 12 hours. The percentages on the figure represent the percentage of DMeOPPV monomer units w/w from which the precursor was formed;

Figure 41 is a graph showing the infra red absorption spectra of a 20% random copolymer of DMeOPPV and PPV in which:

Figure 41a is the precursor

Figure 41b is the copolymer spin-coated on KBr and converted at 220° in vacuo for two hours

Figure 41c is the same sample further converted for two hours at 220°C in the presence of acid;

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Figures 42a, 42b, 42c, 42d, 42e, are graphs showing respectively the infrared absorption spectra of PPV and the random copolymers of PPV, as the major constituent, and DMeOPPV produced from 95 : 5, 90 : 10, 80 : 20 and 70 : 30 molar ratios of PPV and DMeOPPV monomer units respectively;

Figure 43 is a graph showing the absorption spectra of spin-coated thin films of a 20% random copolymer of DMeOPPV and PPV converted in vacuo (a,b) and in the presence of HCl (c,d);

Figure 44 is a graph showing the variation of bandgap with different conversion conditions; the higher bandgap material (a) converted for 2 hours at 220°C in vacuo, the lower bandgap material (b) converted for 12 hours at 100°C in vacuo and subsequently four hours at 220°C in a 15% random copolymer of DMeOPPV and PPV;

Figure 45 is a graph showing the photoluminescence spectra of a 30% random copolymer of DMeOPPV and PPV;

Figure 46 is a graph showing the photoluminescence emission spectra of a 30% random copolymer of DMeOPPV and PPV;

Figure 47 is a graph showing the absorption spectra of capped and uncapped 10% random copolymers of DMeOPPV and PPV; and

Figure 48 is a graph showing the photoluminescence emission spectra of capped and uncapped 10% random copolymers of DMeOPPV and PPV after thermal conversion.

In each of Figures 45 to 48, a film of copolymer were spin-coated and an area was capped with 500Å of evaporated aluminium. The sample was then thermally converted for 12 hours at 220°C in vacuo. The aluminium capping layer was removed by dissolving it in dilute alkali. The lower energy absorption and photoluminescence spectra are from the capped regions of polymer.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Figure 1 illustrates in general terms a process for producing copolymers according to one embodiment of the invention. A mixture of two monomeric bis-sulphonium salts in a suitable solvent was polymerised by reaction with a base. The resultant soluble precursor copolymer was purified and then converted to a conjugated form by heat treatment.

Examples of both the precursor copolymers and the partially conjugated copolymers are shown in the foregoing formulae drawings. The compound of General Formula I represents a precursor copolymer of the compound of General Formula II, which is a poly(para-phenylene vinylene-co-2,5-disubstituted-para phenylene vinylene) copolymer. Similarly, the compound of General Formula III represents a precursor copolymer of the compound of General Formula IV, which is a poly(2,5-thienylene vinylene-co-disubstituted-para-phenylene vinylene) copolymer.

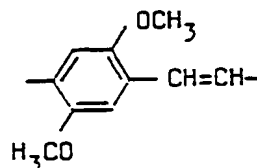
In these compounds the extent of conjugations will be determined by the values of n,m,o and p. Clearly, for a partially conjugated copolymer (II) or (IV),  $o+p \geq 1$ , and so at least some of the vinylic groups will be saturated by inclusion of the modifier group represented by -OR'.

The present invention is concerned in one aspect with improving the efficiency of radiative decay of excitons by trapping them on local regions of the polymer chain, which have lower energy gaps and thus are regions of lower potential energy for the excitons, so that the excitons are confined for a long enough period that they will decay radiatively. This has been achieved by the synthesis of a family of copolymers in which the units which make up the polymer chain are selected from two or more chemically different groups, which

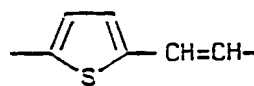
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possess differing bandgaps in their respective homopolymers. Such polymers have been synthesised while still retaining all the desirable processing and materials properties of PPV. In the examples shown in this disclosure, para-phenylene vinylene is used as one of the components (usually the majority component) together with varying compositions of the following other components or their unconverted precursors, as discussed more fully below:

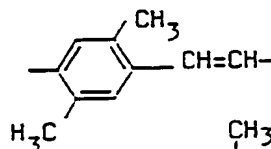
2,5-dimethoxy-para-phenylene vinylene  
(PDMOPV)



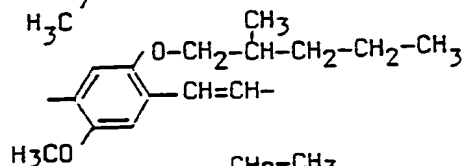
2,5-thienylene vinylene  
(PTV)



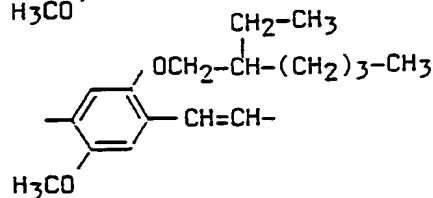
2,5-dimethyl-para-phenylene vinylene  
(PDMPV)



2-methoxy-5-(2'-methylpentyloxy)  
-para-phenylene vinylene  
(MMP-PPV)



2-methoxy-5-(2'ethylhexyloxy)para  
-phenylene vinylene  
(MEH-PPV)



The first three of these components are available in the form of their corresponding homopolymers, and the first two possess an energy gap lower than that of PPV. PPV shows the onset of  $\pi$  to  $\pi^*$  optical transitions at 2.5 eV; poly(2,5-dimethoxy-para-phenylene vinylene), PDMOPV, at 2.1 eV and poly(2,5-thienylene vinylene), PTV, at 1.8 eV. It is expected, on the basis of the known inductive effects of its substituents, that poly(2,5-dimethyl-para-phenylene vinylene), PDMPV, will have a bandgap a little lower than that of PPV.

Dimethyl PPV (DMPPV) has a higher bandgap in its homopolymer than does PPV. This is contrary to the argument which runs that the methyl substituents have inductive effects and so will lower the bandgap of DMPPV over PPV. The true picture is that due to the steric interaction of the dimethyl groups, the polymer conjugated backbone is distorted decreasing the degree of electron delocalisation along the backbone and thus raising the bandgap with respect to PPV. This is evidenced in electron diffraction studies and quantum chemical calculations.

Thus, the copolymers of PPV and DimethylPPV as prepared via a THT leaving group (Figure 8) have a controlled shift in bandgap not because the DMPPV units are saturated giving a copolymer of saturated and unsaturated units but because DMPPV and PPV have genuinely different bandgaps and we are forming a copolymer of the two. We evidence that there are no saturated units by an absence of  $1094\text{cm}^{-1}$  stretch in the FTIR spectra of the precursors. Bandgap is still controllable hence by selection of the monomer units ratio.

There follows specific examples of processes in accordance with embodiments of the invention.

Example 1

A mixture of  $\lambda, \lambda'$ -bis(tetrahydrothiophenium chloride)-p-xylene (0.97 g, 2.8 mmol) and  $\alpha, \alpha'$ -bis(tetrahydrothiophenium chloride)-2,5-dimethoxy-p-xylene (0.12 g, 0.3 mmol) in methanol (7.1 ml) was deoxygenated with nitrogen and cooled with an ice-bath. A nitrogen deoxygenated aqueous sodium hydroxide solution (0.4 M, 2.9 mmol, 7.1 ml) was added dropwise and the reaction mixture was left to stir for 1 hour at 0°C under inert atmosphere. The reaction was terminated by addition of hydrochloric acid (0.4 M, 1.0 ml). The viscous solution was then dialyzed against deoxygenated distilled water (3 x 1000 ml) over 3 days using cellulose membrane dialysis tubing with a molecular weight cut-off of 12,400 (supplied by Sigma Chemical Company Limited, Dorset, U.K.). The solvent was completely removed in vacuo at room temperature from the material remaining in the dialysis tubing. The residue was dissolved in dry methanol (15 ml).

Example 2

A mixture of  $\alpha,\alpha'$ -bis(tetrahydrothiophenium chloride)-p-xylene (0.91 g, 2.6 mmol) and  $\alpha,\alpha'$ -bis(tetrahydrothiophenium chloride)-2,5-dimethyl-p-xylene (0.10 g, 0.26 mmol) in methanol (9.5 ml) was deoxygenated with nitrogen and cooled with an ice-bath. A nitrogen deoxygenated ice-cold aqueous sodium hydroxide solution (0.4 M, 2.9 mmol, 7.1 ml) was added dropwise and the reaction mixture was left to stir for 1 hour at 0°C under inert atmosphere. The reaction was terminated by addition of hydrochloric acid (0.4 M, 0.5 ml). The viscous solution was then dialyzed against deoxygenated distilled water (3 x 1000 ml) over 4 days using cellulose membrane dialysis tubing with a molecular weight cut-off of 12,400 (supplied by Sigma Chemical Company Limited, Dorset, U.K.). The solvent was completely removed in vacuo at room temperature from the material remaining in the dialysis tubing. The residue was dissolved in dry methanol (10 ml).

Example 3

A mixture of  $\alpha,\alpha'$ -bis(tetrahydrothiophenium chloride)-p-xylene (0.98 g, 2.8 mmol) and  $\alpha,\alpha'$ -bis(tetrahydrothiophenium chloride)-2-nitro-p-xylene (0.11 g, 0.33 mmol) in methanol (8.0 ml) was deoxygenated with nitrogen and cooled with an ice-bath. A nitrogen deoxygenated ice-cold aqueous sodium hydroxide solution (0.4 M, 2.9 mmol, 8.0 ml) was added rapidly and the reaction mixture was left to stir for 3.5 hours at 0°C under inert atmosphere. The reaction was terminated by addition of hydrochloric acid (0.4 M, 1.0 ml). The viscous solution was then dialyzed against deoxygenated distilled water (3 x 1000 ml) over 4 days using cellulose membrane dialysis tubing with a molecular weight cut-off of 12,400 (supplied by Sigma Chemical Company Limited, Dorset, U.K.). The solvent was completely removed in vacuo at room

temperature from the material remaining in the dialysis tubing. The residue was dissolved in dry methanol (4 ml).

Example 4 : Preparation of 1-methoxy-4-(2"-methylpentyloxy)benzene

Sodium metal (6.99 g, 304 mmol) was dissolved in dry methanol (120 ml) under Ar to give a 2.5 M solution of sodium methoxide. A solution of 4-methoxyphenol (31.4 g, 253 mmol) in dry methanol (150 ml) was added and this mixture was heated to reflux for 30 min. After cooling to room temperature, a solution of 1-bromo-2-methylpentane (46.0 g, 279 mmol) in dry methanol (100 ml) was added. The mixture was then heated to reflux for 16 hours. The solvent was removed in vacuo, the residue dissolved in ether (200 ml), washed with dilute aqueous sodium hydroxide (250 ml) and water (500 ml), dried over  $\text{MgSO}_4$  and concentrated in vacuo again. Distillation at  $80^\circ\text{C}/0.5$  mm Hg afforded 14.0g (27%)

1-methoxy-4-(2'-methylpentyloxy)benzene,  $^1\text{H}$  NMR (250.1 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 0.94(t, 3 H), 1.02 (d, 3 H), 1.16 - 1.56 (m, 4 H), 1.93 (m, 1 H), 3.64 - 3.82 (m, 2 H), 3.77 (s, 3 H), 6.81 - 6.89 (m, 4 H),  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 14.3, 17.0 (both  $\text{CH}_3$ ), 20.1, 35.8 (both  $\text{CH}_2$ ), 33.0 (CH), 55.7 ( $\text{OCH}_3$ ), 73.9 ( $\text{OCH}_2$ ), 114.6, 115.4 (arom. CH), 153.5, 153.6 (ipso C). IR(film) : 2956(m), 1509(s), 1232(s), 1045(m), 824(m)  $\text{cm}^{-1}$ , MS(EI) : m/z (%) = 208 (100), 124 (32), Calcd. for  $\text{C}_{13}\text{H}_{20}\text{O}_2$  : C 74.96, H 9.68 found : C 75.03, H 9.70.

Example 5: Preparation of 1,4-bis(chloromethyl)-2-methoxy-5-(2'-methylpentyloxy)benzene

A mixture of hydrochloric acid (37%, 59 ml), formaldehyde (39%, 35 ml), 1-methoxy-4-(2'-methylpentyloxy)benzene (14.0 g, 67.4 mmol) and dioxane (100 ml) was saturated with hydrogen chloride for 15 min at  $0^\circ\text{C}$  and stirred for 1.5 hours at room



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temperature. Another 30 ml of formaldehyde was then added at 0°C and hydrogen chloride was bubbled through the reaction mixture for 10 min. After stirring for 16.5 hours at room temperature, the mixture was heated to reflux for 4 hours. The solvents were then completely removed to give a colourless solid residue which was dissolved in a minimum amount of hot hexane (50 ml). This solution was poured into ice-cold methanol (300 ml). The precipitate was filtered under suction and dried to afford 15.5 g (75%) of

1,4-bis(chloromethyl)-2-methoxy-5-(2'-methylpentyloxy)benzene, m.p. 78 - 80°C.  $^1\text{H}$  NMR (250.1 MHz,  $\text{CDCl}_3$ ) :  $\delta$  = 0.92 (t, 3 H), 1.04 (d, 3 H), 1.22 - 1.55 (m, 4 H), 1.95 - 2.05 (m, 1 H), 3.73 - 3.90 (m, 2 H), 3.85 (s, 3 H), 4.62 (s, 2 H), 4.64 (s, 2 H), 6.89 (s, 1 H), 6.92 (s, 1 H).  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ ) :  $\delta$  = 14.3, 17.1 (both  $\text{CH}_3$ ), 20.0, 35.7 (both  $\text{CH}_2$ ), 33.0 (CH), 41.3, 41.4 (both  $\text{CH}_2\text{Cl}$ ), 56.3 ( $\text{OCH}_3$ ), 73.9 ( $\text{OCH}_2$ ) 113.3, 114.1 (arom. CH), 126.8, 127.0, 150.8, 150.9 (ipso C). IR (KBr) : 2958 (m), 1517 (s), 1466 (m), 1414 (s), 1263 (s), 1230 (s), 1036 (s), 734 (s), 696 (s)  $\text{cm}^{-1}$ . MS(EI) : m/z (%) = 304 (18), 220 (38), 84 (41). Calcd. for  $\text{C}_{15}\text{H}_{22}\text{Cl}_2\text{O}_2$  : C 59.02, H 7.26; found : C 58.14, H 6.97.

Example 6: Preparation of 1,4'-bis(tetrahydrothiophenium chloride)-2-methoxy-5-(2'-methylpentyloxy)-p-xylene

Tetrahydrothiophene (20.9 ml, 237 mmol) was added to a suspension of 1,4-bis(chloromethyl)-2-methoxy-5-(2'-methylpentyloxy)benzene (14.5 g, 47.3 mmol) in dry methanol (200 ml). The solid dissolved to form a clear solution within 10 min. This solution was then heated to 50°C for 17 hours. The solvent was completely removed in vacuo, the residue treated with dry acetone, then filtered under suction and dried to give 12.7 g (56%) of 1,4'-bis(tetrahydrothiophenium chloride)-2-methoxy-5-(2'-methylpentyloxy)-p-xylene.  $^1\text{H}$  NMR (250.1 MHz,  $\text{CD}_3\text{OD}$ ) :  $\delta$  = 0.97 (t, 3 H), 1.10 (d, 3 H), 1.26 - 1.61 (m, 4 H), 2.04 (m, 1 H), 2.23 - 2.53 (m, 8 H), 3.55 (br. m, 8 H),

- 32 -

3.86 - 4.05 (m, 2 H), 3.97 (s, 3 H), 4.56 (s, 2 H), 4.57 (s, 2 H), 7.35 (s, 1 H), 7.37 (s, 1 H).  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CD}_3\text{OD}$ ) :  $\delta$  = 14.7, 17.5 ( $\text{CH}_3$ ), 21.1, 29.7, 29.8, 34.3 ( $\text{CH}_2$ ), 36.9 (CH), 43.1, 43.2, 44.5, 44.6, 44.8 ( $\text{CH}_2$ ), 57.1 ( $\text{OCH}_3$ ), 75.8 ( $\text{OCH}_2$ ), 116.5, 117.3 (arom. CH), 121.3, 121.6, 153.0, 153.3 (ipso C). IR (KBr) : 2953 (s), 1514 (s), 1404 (s), 1230 (s), 1033 (s)  $\text{cm}^{-1}$ .

#### Example 7

A mixture of 2,2'-bis(tetrahydrothiophenium chloride)-p-xylene (0.90 g, 2.6 mmol) and 2,2'-bis(tetrahydrothiophenium chloride)-2-methoxy-5-(2'-methylpentylloxy)-p-xylene (0.10 g, 0.21 mmol) in methanol (10 ml) was deoxygenated with argon and cooled with an ice-bath. An argon deoxygenated ice-cold aqueous sodium hydroxide solution (0.4 M, 2.6 mmol, 6.9 ml) was added dropwise and the reaction mixture was left to stir for 1 hour at  $0^\circ\text{C}$  under inert atmosphere. The reaction was terminated by addition of hydrochloric acid (0.4 M, 3.0 ml). The viscous solution was then dialyzed against deoxygenated distilled water (3 x 2000 ml) over 3 days using cellulose membrane dialysis tubing with a molecular weight cut-off of 12,400 (supplied by Sigma Chemical Company Ltd., Dorset, U.K.). The solvent was completely removed in vacuo at room temperature from the material remaining in the dialysis tubing. The residue was dissolved in dry methanol (20 ml). IR spectra of copolymers: Figure 18.

#### Example 8: Preparation of 1-methoxy-4-(2'-ethylhexyloxy)benzene

Sodium metal (6.50 g, 283 mmol) was dissolved in dry methanol (100 ml) under Ar to give a 2.5 M solution of sodium methoxide. A solution of 4-methoxyphenol (29.3 g, 236 mmol) in dry methanol (150 ml) was added and this mixture was heated to reflux for 30 min. After cooling to room temperature, a

solution of 1-bromo-2-ethylhexane (46.5 g, 259 mmol) in dry methanol (150 ml) was added dropwise. The mixture was then heated to reflux for 18 hours. The solvent was removed in vacuo, the residue dissolved in ether (200 ml), washed with dilute aqueous sodium hydroxide (500 ml) and water (500 ml), dried over  $\text{MgSO}_4$  and concentrated in vacuo again. Distillation at  $120^\circ\text{C}/0.1$  mm Hg afforded 24.2 g (43%) 1-methoxy-4-(2'-ethylhexyloxy)benzene.

Example 9: Preparation of 1,4-bis(chloromethyl)-2-methoxy-5-(2'-ethylhexyloxy)benzene

A mixture of hydrochloric acid (37%, 90 ml), formaldehyde (39%, 70 ml), 1-methoxy-4-(2'-ethylhexyloxy)benzene (24.2 g, 101 mmol) and dioxane (120 ml) was saturated with hydrogen chloride for 20 min at  $0^\circ\text{C}$  and stirred for 3 hours at room temperature. Another 50 ml of formaldehyde was then added at  $0^\circ\text{C}$  and hydrogen chloride was bubbled through the mixture for 10 min. After stirring for 3 days at room temperature, the mixture was heated to reflux for 3.5 hours. The solvents were then completely removed to give a pale yellow solid residue which was dissolved in a minimum of hot hexane (75 ml). This solution was poured into ice-cold methanol (300ml). The precipitate was filtered under suction, washed with methanol (200 ml) and dried to afford 21.7 g (63%) of 1,4-bis(chloromethyl)-2-methoxy-5-(2'-ethylhexyloxy)benzene, m. p.  $58 - 60^\circ\text{C}$ . From the mother liquor was obtained another 5.48 g (16%) of bis(chloromethyl)-2-methoxy-5-(2'-ethylhexyloxy)benzene, m. p.  $53 - 55^\circ\text{C}$ .  $^1\text{H}$  NMR (250.1 MHz,  $\text{CDCl}_3$ ) :  $\delta$  = 0.85 - 0.96 (m, 6 H), 1.26 - 1.75 (m, 9 H), 3.74 - 3.86 (m, 2 H), 3.83 (s, 3 H), 4.06 (s, 4 H), 6.89 (s, 1 H), 6.90 (s, 1H). IR (KBr) : 2924 (m), 1516 (s), 1466 (m), 1415 (s), 1263 (s), 1227 (s), 1182 (m), 1032 (s), 733 (m), 700 (s), 614  $\text{cm}^{-1}$  (m).

Example 10: Preparation of  $\lambda, \lambda'$ -bis(tetrahydrothiophenium chloride)-2-methoxy-5-(2'-ethylhexyloxy)-p-xylene

Tetrahydrothiophene (6.4 ml, 72 mmol) was added to a suspension of 2,5-bis(chloromethyl)-1-methoxy-4-(2'-ethylhexyloxy)benzene (4.80 g, 14.4 mmol) in dry methanol (75 ml). The mixture was then heated to 50°C for 22 hours. The solvent was completely removed in vacuo, the residue treated with dry acetone, then filtered under suction and dried to give 4.36 g (59%) of  $\lambda, \lambda'$ -bis(tetrahydrothiophenium chloride)-2-methoxy-5-(2'-ethylhexyloxy)-p-xylene. <sup>1</sup>HNMR (250.1 MHz, CD<sub>3</sub>OD) :  $\delta$  = 0.89 - 1.04 (m), 1.18 (t, J = 7.0 Hz, 3H), 1.29 - 1.65 (m, 8 H), 1.82 (m, 1 H), 2.32 - 2.55 (m, 8 H), 3.50 - 4.56, 4.57 (both s, 2 H, CH<sub>2</sub>Cl), 7.38 and 7.39 (both s, 1 H, arom. H). IR (KBr) : 2948 (broad, m), 1514 (s), 1460 (m), 1399 (s), 1312 (m), 1229 (s), 1033 (s), 703 cm<sup>-1</sup> (m).

Example 11

A mixture of  $\lambda, \lambda'$ -bis(tetrahydrothiophenium chloride)-p-xylene (0.92 g, 2.6 mmol) and  $\lambda, \lambda'$ -bis(tetrahydrothiophenium chloride)-2-methoxy-5-(2'-ethylhexyloxy)-p-xylene (0.11 g, 0.22 mmol) in methanol (10 ml) was deoxygenated with argon and cooled with an ice-bath. An argon deoxygenated ice-cold aqueous sodium hydroxide solution (0.4 M, 2.6 mmol, 6.5 ml) was added dropwise and the reaction mixture was left to stir for 2.5 hours at 0°C under inert atmosphere. The reaction was terminated by addition of hydrochloric acid (0.4 M, 0.8 ml). The viscous solution was then dialyzed against deoxygenated distilled water (3 x 2000 ml) over 3 days using cellulose membrane dialysis tubing with a molecular weight cut-off of 12,400 (supplied by Sigma Chemical Company Ltd, Dorset, U.K.). The solvent was completely removed in vacuo at room temperature from the material remaining in the dialysis tubing. The residue was dissolved in dry methanol (20 ml). IR spectra of copolymers: Figure 22.

Example 12

A solution of 1,4-bis(chloromethyl)-2-methoxy-5-(2'-ethylhexyloxy) benzene (0.95 g, 2.9 mmol) and  $\alpha, \alpha$ '-dichloro-p-xylene (0.05 g, 0.29 mmol) in dry tetrahydrofuran (20 ml) was added to a solution of potassium tert-butoxide (95%, 2.5 g, 22 mmol) in dry tetrahydrofuran (120 ml) over 15 min. The mixture was then stirred at room temperature for 21.5 hours. The resulting orange mixture was reduced to 10% of its volume and poured into methanol (500 ml). The precipitate was filtered under suction and recrystallised from tetrahydrofuran/methanol to afford 101 mg of polymer.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ) : Figure 24. IR spectra of copolymers: Figure 25.

The absorption spectra of MEH-PPV, 5% PPV/95% MEH-PPV and 20% PPV/80% MEH-PPV are shown in Figure 26. The photoluminescent spectra (Figure 27a, 26b, 31a) show that the luminescence is as expected of higher energy with increasing number of PPV units. EL devices were made in a standard configuration with ITO and aluminium contacts and the material showed electroluminescence (Figure 29a, 29b, 30a and 30b). The corresponding electroluminescence spectra are illustrated in Figure 28a and 28b. Both the 5% PPV/95% MEH-PPV and the 20% PPV/80% MEH-PPV had a turn-on voltage of about 8 V.

Example 13

The previous PPV EL devices were constructed with PPV prepared via a Tetrahydrothiophenium (THT)-leaving precursor polymer (Figure 32a) spun from methanolic solution. This precursor is unstable with respect to its conjugated product and is fully converted by heating at 220°C for 2 hours (Figure 32c).

By replacing the THT-leaving group with a methoxy (MeO)-leaving group a more stable precursor (Figure 32b) is formed. This can be easily processed by spin coating from a solution in chloroform (as can the THT-precursor from methanolic solution). Thermal conversion of the MeO-leaving PPV precursor at 300°C in vacuo for 12 hours gives very little thermal elimination leaving a copolymer of conjugated and unconjugated units (Figure 32d). This is clearly seen from the absorption spectra of the THT-leaving PPV and the MeO-leaving PPV (Figure 33). The absorption spectra of the precursors of both are very similar. A significant change occurs in the absorption spectrum of the THT-leaving PPV (Figure 34); an insignificant change occurs in the absorption spectrum of the MeO-leaving PPV (Figure 35). Clearly both products are subsequently very stable against subsequent changes at room temperatures and are very suitable as emitting materials in commercial EL devices.

A device was made with the MeO-leaving PPV. An ITO substrate was cleaned in an ultrasound bath, of first acetone and subsequently propan-2-ol. The precursor material was then spin-coated on the substrate. The device was then thermally converted at 300°C in vacuo for 12 hours. A top contact of Aluminium was then deposited to define an active area by vacuum deposition at a pressure of less than  $6.10^{-6}$  torr to a thickness of 2-500Å.

The performance of the device shows no deterioration over those made with PPV prepared via a THT leaving group precursor polymer with a turn on voltage below 10V, a diodic current-voltage characteristic and a largely linear current-luminance response and a slightly improved quantum efficiency by at least a factor of 2 (Figures 36 and 37).

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The emission spectrum of the MeO-leaving PPV is markedly different with a peak emission at 2.5eV compared with 2.25eV in THT-leaving PPV. The emission is a bluey-green as opposed to a greeny-yellow in the case of the THT-leaving PPV. This is again consistent with the MeO-leaving PPV as converted being a copolymer of conjugated and unconjugated sequences: emission coming from the small conjugated sequences but at a higher energy than in fully conjugated PPV, (Figure 37).

Thus by careful conversion conditions it is possible using copolymers of PPV to obtain electroluminescent emission of different colours and with improved efficiencies.

#### Example 14

The random copolymers of PPV and DMeOPPV give a means to controlling the bandgap of a conjugated polymer and the potential for the construction of multicolour EL devices and channel waveguides.

The copolymers are prepared initially in a precursor form which is soluble in Methanol and consists of at least 3 distinct monomer units - a PPV precursor monomer unit with a THT-leaving group, a DMeOPPV monomer unit with a THT-leaving group and certainly a DMeOPPV monomer unit with a MeO-leaving group (formed by the methanolic solution substitutionally attacking the DMeOPPV THT-leaving units) as seen by the strong  $1094\text{cm}^{-1}$  adsorption in the infrared absorption spectra of both the MeO-leaving homopolymer precursor of DMeOPPV and all the copolymer precursor polymers. There is possible a small amount of a fourth monomeric unit- a PPV monomer unit with a MeO-leaving group (formed by the methanolic solution substitutionally attacking the PPV THT-leaving units) (Figure 39(a)).

Thin films (of the order of 1000Å as used in EL devices) of the copolymers can be obtained by spin-coating the precursor solutions. Thermal conversion of the said films gives mechanically and thermally robust films. It is found that by linearly varying the copolymer monomer unit ratio that the absorption edge of the converted copolymers may be accurately controlled (Figure 40). Typically films are converted at 220°C for 2 hours. More fully conjugated material has a lower bandgap. The controlled increase in bandgap with additional DMeOPPV to PPV units indicates an associated decrease in conjugation. FTIR data shows that the copolymers are only partially conjugated as converted (Figure 41). There is still a significant absorption at 1094cm<sup>-1</sup> indicating monomeric units of DMeOPPV with the methoxy leaving group have not been converted to the conjugated form leaving a copolymer of conjugated sequences and unconjugated sequences. The degree of conjugation will thus vary with the number of DMeOPPV Units present (Figure 42).

To convert fully the homopolymer of DMeOPPV with the methoxy leaving group it is necessary to heat the precursor in the presence of acid to catalyse the loss of the methoxy group. As the THT-leaving group leaves, acid is also generated. Thus in the copolymers of PPV and DMeOPPV it is possible further to convert the monomeric units of DMeOPPV with the methoxy leaving group to the conjugated form, so lowering the bandgap further and giving more control of the bandgap, by methods of internally trapping the self produced acid where excess acid may damage electrodes or simply by heating the precursor films in the presence of acid.

By converting a spun-coated film of a copolymer at 220°C in an argon flow which has been passed through concentrated HCl for 2 hrs it is clearly seen that the absorption bandgap of the polymer is shifted to lower energy over a similar film



converted at 220°C in vacuo indicating that the "acid" converted film is more fully conjugated. FTIR absorption measurements support this with the disappearance of the 1094cm<sup>-1</sup> absorption only when the copolymer is "acid" converted. Again it is noted that 2 hours conversion by either technique gives stable material against further change (Figures 43 and 41).

By converting a spun-coated copolymer film on a glass substrate initially with a low temperature bake in vacuo at about 100°C the diffusion rate of the acid ions out of the film is reduced giving an enhanced probability of causing conversion of methoxy-leaving units. A subsequent bake at 220°C in vacuo yields fully stable material at room temperature again. A considerable reduction in bandgap is so obtained over material heated directly to 220°C in vacuo. Thus there is a further method for controlling the bandgap of these materials (Figure 44).

It should be emphasised that any method of controlling the bandgap in these conjugated polymers equally controls the colour of emitted light in an electroluminescent device (or the colour of photoluminescence under optical excitation) as the wavelength of the emitted light largely follows the bandgap of the material (an increase in the bandgap of the material causes a similar decrease in the wavelength of the emitted light). The spatial limit for this spatial control of bandgap across the polymer film is of the order of the thickness of the polymer film i.e. 1000Å.

Another film of copolymer (30% Copolymer) was spun-coated onto a glass substrate and before thermal conversion 500Å of Aluminium were vacuum deposited at a pressure of less than 6.10<sup>-6</sup> torr via a shadow mask. The sample was then baked in vacuo for 20 hours at 220°C to facilitate full conversion. The sample was then etched in weak sodium hydroxide solution

to remove the aluminium. The polymer film was unaffected by the etching process. However, the polymer is left patterned. Where the aluminium was, the polymer to the eye is a deeper orange colour indicating a greater degree of conjugation due to enhanced trapping of the acid ions in the polymer film by the aluminium. This is born out by the shift to lower energy of the absorption edge (Figure 45) and the photoluminescence emission (Figure 46) of the dark region originally covered by the aluminium. Thus the bandgap of the copolymers may again be controlled and moreover in different regions of the same film giving rise to the possibility of multicolour emission from a single EL device.

Such patterning also has an application in the manufacture of channel waveguides. Another such patterned device as above was made (from 10% copolymer) and there were the same associated lowering of bandgap and absorption edge where the aluminium had been etched from (Figure 47) and lowering in energy of the photoluminescence emission from the same area (Figure 48). The refractive indices of the two regions at 633nm were measured by coupling light into the first TE modes from a He-Ne laser. The refractive index of the less conjugated material was measured to be 1.564 (0.002) and that of the more conjugated material (as converted under the encapsulation of aluminium) was measured to be 1.620 (0.002). This result is in keeping with simple dispersion theory for propagation of light in a dielectric medium such that the refractive index varies inversely with bandgap. Thus the patterning of the polymer allows also the spatial control of refractive index across a polymer film to a length scale of the order of 1000Å. For typical waveguiding structures (such as a channel waveguide) it is necessary to define channels of material to a precision of the order but no smaller than the wavelength of the light to be guided (i.e. for the 633nm emission from a He-Ne laser to a precision of the order of 6000Å) with a higher refractive index than of the surrounding

material. Clearly this method of patterning the copolymers of PPV and DMeOPPV is amenable to making waveguide structures as high refractive index regions can be defined to a size smaller than the wavelength of light which is to be confined in the high index region and guided.

In order to characterise more fully the nature of the resulting copolymers the absorption spectra were obtained from samples which had been spun onto glass under the same conditions as discussed below for the construction of devices (step (c)) and subsequently thermally converted side by side with the corresponding devices (step (d)). The results thus provide a direct insight into the effect upon the polymer electronic structure of the copolymer composition. Figure 2a shows a set of spectra for the compositions of the copolymers (of general structure II with  $R = OCH_3$ ) of para-phenylene vinylene, 2,5-dimethoxy-para-phenylene vinylene and unconverted precursor units that have been investigated in device structures and whose performance is exemplified below. The spectra have all been scaled to the same peak absorption to allow a ready comparison of the onsets for their  $\pi$  to  $\pi^*$  optical transitions and the energies of their absorption peaks. Also shown for comparison is the absorption spectrum of the PDMOPV homopolymer obtained as previously shown in "Polyarylene vinylene films prepared from precursor polymers soluble in organic solvents", S. Tokito *et al*, Polymer 31, 1137 (1990). There is a clear trend in these spectra that the energy of the absorption peak shifts to higher energy as the relative content, in the precursor copolymer (structure I with  $R = OCH_3$  and  $R^1, R^2 = -(CH_2)_4-$ ), of units of the precursor to 2,5-dimethoxy-para-phenylene vinylene is increased. This behaviour is contrary to expectation for a fully conjugated copolymer since as discussed above and shown in Figures 2a and 2b, PDMOPV has a lower energy gap than PPV. In Figure 2a, curve (a) is 100% PPV, (b) is 95% PPV/5% PDMOPV, (c) is 90% PPV/10% PDMOPV, (d) is 85% PPV/15% PDMOPV, (e) is

80% PPV/20% PDMOPV and (f) is 70% PPV/30% PDMOPV. Similarly this has been observed with 95% PPV/5% MMP-PPV, 90% PPV/10% MMP-PPV and 80% PPV/20% MMP-PPV (Figure 19) and with 95% PPV/5% MEH-PPV, 90% PPV/10% MEH-PPV and 80% PPV/20% MEH-PPV (Figure 23). The data is however consistent with incomplete conversion of the precursor units during the thermal treatment, resulting in remnant non-conjugated sequences that interrupt the  $\pi$ -electron delocalisation (structure II with  $R = OCH_3$ ), limiting the effective conjugation length and thus increasing the  $\pi$  to  $\pi^*$  transition energy. These remnant sequences are mostly associated with the precursor to 2,5-dimethoxy-para-phenylene vinylene however, there can also be methoxy leaving groups associated with the precursor to PPV, i.e. the methoxy leaving group precursor polymer to PPV, which will not be fully eliminated by thermal treatment (structure II with  $R = OMe$ ). The lack of conversion of the methoxy precursors to 2,5-dimethoxy-para-phenylene vinylene and to para-phenylene vinylene under the thermal conversion procedure utilised here is ascribable to the difficulty of elimination of the methoxy leaving group, previously shown in "Polyarylenevinylene films prepared from precursor polymers soluble in organic solvents" S. Tokito, T. Momii, H. Murata, T. Tsutsui and S. Saito, Polymer 31, 1137 (1990) to require acid catalysis for its full removal. It should be emphasised that while the conversion of the precursors to PPV does in fact liberate acid as one of its by-products, in thin film copolymer samples converted by heating in vacuo the acid is too rapidly removed to be effective in driving the conversion of the precursor to 2,5-dimethoxy-para-phenylene vinylene to completion. In thick film samples prepared by static solution casting, however, the extent of conversion of the methoxy precursors is significantly enhanced. This is clearly evidenced in their colour (they are unfortunately too thick for optical absorption measurements) which, unlike the uniformly yellow thin film samples, becomes increasingly red as the content of the precursor to 2,5-dimethoxy-para-

phenylene vinylene in the copolymers increases. It is also evidenced by the decrease of the strength, during conversion, of the characteristic C-O stretch vibration in the infrared spectra that is associated with the methoxy modifier group on the benzylic carbon of the methoxy precursors to 2,5-dimethoxy-para-phenylene vinylene and para-phenylene vinylene. This behaviour can be understood as being due to the lower rate of loss of acid from the bulk of thick films, allowing greater interaction with the units of the methoxy precursors and consequently a greater extent of their conversion. Further evidence supporting these differences between the thin, spin-coated films and thicker solution cast films comes from their photoluminescence spectra. Discussion here is limited to the representative cases of the copolymers obtained following thermal conversion of thin spin-coated and thick solution cast films of the copolymer precursors prepared from (1) 10% of units of the precursor to 2,5-dimethoxy-para-phenylene vinylene/90% of units of the precursor to para-phenylene vinylene and (2) 20% of units of the precursor to 2,5-dimethoxy-para-phenylene vinylene/80% of units of the precursor to para-phenylene vinylene. In Figure 3(a) and (b) are shown respectively the emission spectra for thin spin-coated and thick solution cast films for case (1). In Figure 4(a) and (b) are shown the corresponding spectra for case (2). For comparison Figures 5(a) and (b) show the photoluminescence spectra for the PPV and PDMOPV homopolymers; the latter prepared via acid catalysed thermal conversion under HCl containing nitrogen gas flow so as to ensure substantial, if not wholly complete, conversion of the precursor units. It is immediately clear from the spectra in Figures 3 and 4 that in vacuo thermally converted spin-coated thin films have significantly different emission spectra to the thicker films obtained under identical conversion conditions and from the same precursor solutions but following static solution casting. Furthermore, whilst the spectra of the thin spin-coated samples have spectra which lie at higher

energy than in PPV (Figure 5(a)), the thicker static solution cast samples show spectra that are red shifted relative to PPV and hence that are shifting towards the emission spectrum seen in PDMOPV (Figure 5(b)).

It is thus clear that the electronic structures of the copolymers that are incorporated into device structures may be controlled by the selection of the constituent components present in the copolymer precursor and by the conversion conditions used in device fabrication. Changing some of the units of the precursor to para-phenylene vinylene to units of the precursor to 2,5-dimethoxy-para-phenylene vinylene can have two different effects depending on whether conversion is purely thermal or also involves acid catalysis. For purely thermal conversion there is an incomplete elimination such that the resultant conjugated segments are separated by remnant non-conjugated precursor units, causing the energy gap to increase relative to that of homopolymer PPV and the photoluminescence emission to be blue shifted, occurring at higher energy than in PPV. For acid catalysed thermal conversion the elimination is substantially complete with the result that the energy gap decreases and photoluminescence emission shifts to the red.

A similar situation arises in the case of the copolymers of the precursor to para-phenylene vinylene and the precursor to 2,5-thienylene vinylene (structure II with  $R = H$  and  $R' = CH_3$ ) with the absorption spectra of thin spin-coated films of in vacuo thermally converted copolymers showing a shift in the position of the absorption peak to higher energy than seen in PPV (see Figure 6) whilst the photoluminescence emission spectra for thick solution cast films converted under identical conditions show a red shift relative to that in PPV (see Figure 7 (a), (b) and (c)). In Figure 6, curve (a) is 100% PPV, (b) is 95% PPV/5% PTV and (c) is 90% PPV/10% PTV. Thus, the conversion of methoxy modifier group precursor units of 2,5-thienylene vinylene is enhanced in thick films by acid

catalysed elimination driven by the acid by-product of the para-phenylene vinylene sulphonium-salt-precursor conversion. It was previously reported in "Optical Excitations in Poly(2,5-thienylene vinylene)", A.J. Brassett, N.F. Colaneri, D.D.C. Bradley, R.A. Lawrence, R.H. Friend, H. Murata, S. Tokito, T. Tsutsui and S. Saito, Phys. Rev. B 41, 10586 (1990) that the photoluminescence emission from the PTV homopolymer obtained by acid catalysed thermal conversion of the methoxy leaving group precursor polymer is extremely weak (with quantum yield less than or of order  $10^{-5}$ ) and, when it can be observed, appears at energies above the onset for  $\pi$  to  $\pi^*$  optical transitions.

In the copolymers of the precursors to para-phenylene vinylene and 2,5-dimethyl-para-phenylene vinylene (structure (I) with  $R = \text{OCH}_3$  and  $R^1, R^2 = -(\text{CH}_2)_4-$ ) the absorption spectra of in vacuo thermally converted thin spin-coated samples show a shift in the position of the absorption peak to higher energy than seen in PPV (see Figure 8) whilst the photoluminescence emission spectra for thick solution cast films converted under identical conditions show little shift relative to that in PPV (see Figure 9(a), (b) and (c)). In Figure 8, curve (a) is 100% PPV, (b) is 95% PPV/5% DMPPV and (c) is 90% PPV/10% DMPPV. The explanation of the higher bandgap energy observed in the absorption spectra of the thin spin-coated samples is that the as-formed copolymer contains disruption in the conjugation due either to steric interactions of the methyl group with the vinylic proton twisting the  $\text{sp}^2$ - $\pi$ -orbitals of the dimethyl-para-phenylene and the adjacent vinylene units out of planarity or that in the absence of acid catalysed conversion, the elimination of methoxy leaving groups from the methoxy precursors to 2,5-dimethyl-para-phenylene vinylene and para-phenylene vinylene is incomplete, thus resulting in a copolymer structure containing conjugated segments separated from each other by unconverted non-conjugated precursor units or a combination of both.

The inventors have trapped some of the acid released from a thin film during thermal conversion by capping a section of a film of the 10% dimethoxy-PPV/90% PPV precursor polymer which had been spin coated onto a glass slide (about 2.5 cm square) with a strip of evaporated aluminium (about 4 mm wide) before heat treatment. The precursor was then heated as described above to leave a film of thickness 100 nm and the aluminium was removed using dilute aqueous sodium hydroxide. There was a clear difference in colour between the area previously coated with aluminium (orange) and that where there had been no aluminium (yellow). The optical absorption spectra for the two areas are shown in Figure 16 from which it can be seen that there is a shift in band gap towards the red of about 0.2 eV for the area previously coated with aluminium. The photoluminescent spectra for the two regions are shown in Figure 17. This shows that we can control the extent of conjugation in different regions of the same polymer film so as to produce different emission colours from these different regions.

#### Fabrication of Electroluminescent (EL) Structures

Structures for an EL device require two electrodes to either side of the emissive region. For the examples shown here, devices have been fabricated by deposition of a series of layers onto a transparent substrate (glass), but other structures can also be made, with the active (i.e. emissive) area being defined by patterning within the plane of the polymer film.

The choice of electrode materials is determined by the need to achieve efficient injection of charge carriers into the polymer film, and it is desirable to choose materials which preferably inject electrons and holes as the negative and positive electrodes respectively. In International Patent Application No. PCT/GB90/00584 (Publication No. PCT/WO9013148)



is described the use of PPV as the emissive layer, and a choice of aluminium, amorphous silicon, silver/magnesium alloy as the negative electrode, and aluminium with a thin oxide coating, gold and indium oxide as the positive electrode. Many of these combinations were found to be satisfactory. In the present disclosure, where many different compositions of copolymers have been investigated, the choice of contact layers has been generally for convenience that of aluminium for the negative electrode and aluminium with an oxide coating as the positive electrode. Calcium has also been used as the negative electrode with indium/tin oxide as the positive electrode. It is to be expected that results obtained with this combination give a good indication of the behaviour to be expected with other choices for electrode materials:

The procedure used for all devices used in this work is as follows:

- (a) Clean glass substrates (microscope slides) in propan-2-ol reflux.
- (b) Deposit bottom contact of aluminium by evaporation of aluminium in a standard vacuum evaporator (base pressure  $2 \times 10^{-6}$  mbar). Four strips 1mm wide were usually deposited, and the aluminium film thickness was chosen to give a conducting but semi-transparent film (9-12nm). The aluminium was then exposed to air at room temperature, to allow formation of a surface oxide coating.
- (c) Deposition of the precursor polymer from solution in methanol by spin-coating, using a Dyna-Pert PRS14E spin-coater. This was performed inside a laminar-flow cabinet, with a spin speed of 2000 rev/min, and produced films of polymer in the thickness range 50-150nm.
- (d) Thermal treatment of the precursor, to convert to the conjugated polymer. This was carried out in an evacuated

oven (base pressure  $10^{-5}$  mbar) inside an argon-atmosphere glove box. The heat treatment used was 30 min to heat to  $220^{\circ}\text{C}$ , between 2 and 5 hours at  $220^{\circ}\text{C}$ , and 3 hours to cool to room temperature.

(e) Evaporation of aluminium top contact, carried out as in (b) above, but with the 1mm wide strips rotated by  $90^{\circ}$ , to give a total of 16 independently addressable devices, each  $1\text{mm}^2$ . The aluminium thickness here was typically 50nm, to ensure a good coverage, and to provide some encapsulation to keep oxygen away from the active parts of the device.

#### Measurements of Devices

Positive bias was applied to the bottom contact (aluminium with surface oxide coating) using a programmable voltage source (Keithley model 230). The current through the device was measured with a Keithley model 195 DVM connected between the top contact and ground. The light output was measured with a large area silicon photovoltaic cell ( $1\text{cm}^2$  active area, Radio Spares catalogue number RS 303-674).

Typical results of the PPV homopolymer, a copolymer obtained by in vacuo thermal conversion of spin-coating thin films of spin coated films of a precursor copolymer synthesised from 90% para-phenylene vinylene/10% 2,5-dimethoxy-para-phenylene vinylene precursor units, a copolymer obtained by in vacuo thermal conversion of spin-coated thin films of a precursor copolymer synthesised from 90% para-phenylene vinylene/10% 2,5-thienylene vinylene precursor units and a copolymer obtained by in vacuo thermal conversion of spin-coated thin films of a precursor copolymer synthesised from 90% para-phenylene vinylene/10% 2-methoxy-5-(2'-methylpentyloxy)-para-phenylene vinylene precursor units are shown in Figures 10, 11, 12, 20 and 21 which present the current versus voltage and light output versus current characteristics. In Figure 10

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the bottom contact thickness is 110Å, the top contact thickness is 1300Å and the thickness of the electroluminescent layer is 900Å. In Figure 11 the corresponding thickness values are 120Å, 1000Å and 1450Å and in Figure 13 they are 90Å, 1370Å and 1070Å. Similar current versus voltage characteristics were found for all devices, with a threshold voltage for current injection of around 25 to 40V. There was also found a broadly linear relation between current and light output (which allows the efficiency of the device to be characterised simply, by the gradient of this plot).

It is found that the light output varies strongly with the choice of copolymer, and that some of the copolymers show very strongly enhanced efficiencies as measured against the efficiency of the PPV homopolymer. The variation of the quantum efficiency is shown as actually measured (current in photodetector/current through EL device) in Figures 13, 14, 15 and 31 for the copolymers obtained from the in vacuo thermal conversion of spin-coated thin films of precursor copolymers formed between the precursors to PPV and PDMOPV, the precursors to PPV and PTV, the precursors to PPV and PDMPV, and the precursors to PPV and MMP-PPV respectively. The plots show some data for a large number of devices, and there is some scatter evident between devices of the same nominal composition. This may be due to inhomogeneities in the devices, such as non-uniform thickness, entrapped dust particles etc. and it is considered that the better values of efficiency at each composition give a true indication of the intrinsic behaviour of the EL structure. The PPV/PDMOPV copolymers show a very big improvement in efficiency for PDMOPV in the range 5-15%, with best results at 10%, for which the improvement over that obtained for PPV is by a factor of about 50. The PPV/PTV copolymers do not show such behaviour. This may be compared with the very low quantum yield for photoluminescence (less than or of order  $10^{-5}$ ) that is found in the homopolymer, as in "Optical Excitations in

Poly(2,5-thienylene vinylene)", A.J. Brassett, N.F. Colaneri, D.D.C. Bradley, R.A. Lawrence, R.H. Friend, H. Murata, S. Tokito, T. Tsutsui and S. Saito, Phys. Rev. B 41, 10586 (1990). For the PPV/PDMPV copolymers an improvement over the PPV homopolymer is seen at 10% PDMPV, but the changes are less marked than with the PPV/PDMOPV copolymers.

The maximum measured efficiencies for the devices shown here, obtained for the 90/10% PPV/PDMOPV copolymer, approach  $10^{-2}\%$ . To obtain the real efficiency of the EL layer in the device it is necessary to correct for the efficiency of the photodetector (50%), the collection efficiency for the EL (24%) and the optical transmittance of the Al semitransparent layer (30%). With these factors included, it is estimated that the real efficiency of the EL layer in such a device is as high as 0.3%. This value compares very favourably with the performance of EL devices fabricated with other materials.

As PL and EL are due to the same excited state in the polymer, as evidenced by the similarity in emission recorded for a single polymer film, a correspondence between efficiency for EL and for PL is broadly to be expected. However, there are some differences as discussed below.

The efficiency for luminescence is in part an intrinsic property of the material (that is to say that it has the same value for all samples), and possibly also dependent on the actual form of the sample and the nature of the interfaces to it. Thus, it might be expected for the thin films used for the EL structures that migration of the excited states to the interface between the polymer film and the electrode material might result in non-radiative decay of the excited state, and thus allow the efficiency for luminescence to fall below its "intrinsic" value. The effect, then of restricting the motion of the excited states in the copolymers may be to improve quantum yield both by improving the intrinsic properties of

the polymer, and also by reducing the motion of excited states to the interface region. Thus, the improvements in quantum yield that have been measured in EL for some of the copolymers are by a very large factor ( $\times 50$ ), considerably larger than the factor by which the yield for PL is improved.

There has been described a design technique and a method of manufacture for achieving especially efficient emission in conjugated copolymer electroluminescent structures through the use of the local modulation of semiconductor energy gap, between the highest occupied and lowest unoccupied energy levels, achieved in copolymers of two or more different monomer units. The modulation of energy gap is achieved by the use, in the copolymer structure, of chemically-different monomer units which in their individual homopolymer forms have different energy gaps. The effect of the energy gap modulation is to produce local regions that are potential energy minima and that act to confine the exciton states created by injection of electrons and holes from the contact layers. This confinement is beneficial for efficient radiative recombination of excitons through its reduction of the opportunities for migration of the excitons to non-radiative recombination sites subsequent to their initial generation and thus leads to a higher electroluminescent yield.

The copolymers described herein are intractable, insoluble in common solvents and infusible at temperatures below the decomposition temperature, or they are soluble in a few organic solvents.

CLAIMS:

1. A semiconductive conjugated copolymer comprising at least two chemically different monomer units which, when existing in their individual homopolymer forms, have different semiconductor bandgaps, the proportion of said at least two chemically different monomer units in the copolymer having been selected to control the semiconductor bandgap of the copolymer so as to control the optical properties of the copolymer, said copolymer having been formed in a manner enabling it to be laid down as a film without substantially affecting the luminescent characteristics of the copolymer, said copolymer being stable at operational temperature.
2. A copolymer as claimed in claim 1, wherein the semiconductor bandgap has been spatially modulated so as to increase the quantum efficiency of the copolymer when excited to luminesce.
3. A copolymer as claimed in claim 1 or claim 2, wherein the semiconductor bandgap has been spatially modulated so as to select the wavelength of radiation emitted during luminescence.
4. A copolymer as claimed in any one of claims 1 to 3, wherein the semiconductor bandgap has been spatially modulated so as to select the refractive index of the copolymer.
5. A copolymer as claimed in any one of the preceding claims, wherein the chain of the copolymer is fully conjugated.
6. A copolymer as claimed in any one of the claims 1 to 4, wherein at least one of the monomer units is not fully conjugated in the chain of the copolymer.

7. A copolymer as claimed in claim 6, which is a conjugated poly(arylene vinylene) copolymer in which a proportion of the vinylic groups of the copolymer are saturated by inclusion of a modifier group substantially stable to elimination during formation of the film, the proportion of saturated vinylic groups controlling the extent of conjugation, thereby spatially modulating the semiconductor bandgap of the copolymer.
8. A poly(arylene-1,2-ethanediyl) precursor copolymer wherein a proportion of the ethane groups include a modifier group substituent and at least some of the remaining ethane groups include a leaving group substituent, the precursor copolymer being convertible by elimination of the leaving group substituents into a copolymer as defined in claim 7.
9. A copolymer as claimed in claim 8, wherein the leaving group substituent comprises a sulphonium salt.
10. A copolymer as claimed in any one of claims 7 to 9, wherein the modifier group is an alkoxy group.
11. A copolymer as claimed in claim 10, wherein the alkoxy group is a methoxy group.
12. A copolymer as claimed in any one of claims 7 to 11, wherein the arylene moieties of the copolymer chain have as a first component para-phenylene and a second component selected from the group comprising: 2,5 dimethoxy-para-phenylene; 2,5-thienylene; 2,5 dimethyl-para-phenylene; 2-methoxy-5-(2'-methylpentyloxy)-para-phenylene; and 2-methoxy-5-(2'-ethylhexyloxy)-para-phenylene.
13. A copolymer as claimed in claim 12, wherein para-phenylene comprises at least 70 mole % of the total amount of arylene present.

14. A copolymer as claimed in claim 12, wherein para-phenylene constitutes an amount in the range 85-95% and wherein the second component is 2,5 dimethoxy-para-phenylene.

15. A conjugated semiconductive copolymer comprising an amount of poly(p-phenylene vinylene) in the range 90-95% and an amount of poly(2,5-dimethyl-phenylene vinylene) in the range 5-10%.

16. A conjugated semiconductive copolymer of poly(p-phenylene vinylene) and poly (p-phenylene 1-methoxy-1,2 ethanediyl) comprising at least 20% poly (p-phenylene vinylene).

17. A copolymer as claimed in any one of claims 1 to 7, wherein at least one of the monomer units comprises an arylene vinylene unit substituted with a solubilizing group in the arylene ring so as to render the copolymer soluble.

18. A copolymer as claimed in claim 17, wherein the solubilizing group comprises an alkoxy group of at least four carbon atoms.

19. A copolymer as claimed in claim 18, wherein the alkoxy group is a 2-methylpentyloxy group or a 2-ethylhexyloxy group.

20. A method of forming a conjugated poly(arylene vinylene) copolymer as defined in claim 7, which method comprises heating substantially in the absence of oxygen a poly(arylene-1,2- ethanediyl) precursor copolymer wherein a proportion of the ethane groups include a modifier group substituent and at least some of the remaining ethane groups include a leaving group substituent, whereby elimination of the leaving group substituents occurs substantially without elimination of the modifier group substituents so as to form the conjugated poly(arylene vinylene) copolymer.



21. A method as claimed in claim 20, wherein the heating is carried out in a temperature range of 70-300°C.
22. A method as claimed in claim 20 or 21, wherein the heating is carried out under acidic catalysis.
23. A method as claimed in any one of claims 20 to 22, which further comprises a first step of forming the poly(arylene-1,2-ethanediyl) precursor copolymer, which step comprises reacting a first monomer component with a second monomer component, in the presence of base and a solvent comprising the modifier group, wherein the first monomer component comprises a first arylene moiety substituted with  $-\text{CH}_2\text{L}^1$  and  $-\text{CH}_2\text{L}^2$  and the second monomer component comprises a second arylene moiety substituted with  $-\text{CH}_2\text{L}^3$  and  $-\text{CH}_2\text{L}^4$ , in which  $\text{L}^1$ ,  $\text{L}^2$ ,  $\text{L}^3$  and  $\text{L}^4$  each represents a leaving group substituent which may be the same or different from one another.
24. A method as claimed in claim 23, wherein the solvent includes water.
25. A method as claimed in claim 23 or claim 24, wherein the solvent comprises at least 30% modifier group by weight.
26. A method as claimed in any one of claims 23 to 25, wherein the temperature of the first step is in the range -5°C to 10°C.
27. A method as claimed in any one of claims 23 to 26, wherein the reaction time does not exceed 4 hours.
28. A method as claimed in any one of claims 23 to 27, which further comprises a second step of purifying the precursor copolymer before the heating.

29. A method as claimed in any one of claims 23 to 28, wherein the or each leaving group substituent comprises a sulphonium salt.

30. A method as claimed in any one of claims 23 to 29, wherein the modifier group comprises an alkoxy group.

31. A method as claimed in claim 30, wherein the alkoxy group is a methoxy group.

32. A method as claimed in any one of claims 23 to 31, wherein the arylene moieties of the copolymer chain have a first component comprising para-phenylene and a second component selected from the group comprising: 2,5 dimethoxy-para-phenylene; 2,5 thienylene; 2,5 dimethyl-para-phenylene; 2-methoxy-5-(2'-methylpentyloxy)-para-phenylene; and 2-methoxy-5-(2'-ethylhexyloxy)-para-phenylene.

33. A method as claimed in claim 32, wherein the para-phenylene in monomer form comprises at least 70 mole % of the total amount of monomer present in the first step.

34. A method of forming a conjugated poly(arylene vinylene) copolymer as claimed in claim 7, which method comprises heating substantially in the absence of oxygen a poly(arylene-1,2-ethanediyl) precursor polymer wherein at least some of the ethane groups include a modifier group substituent, the heating condition being controlled so that elimination of the modifier group substituents occurs to form the copolymer whereby a proportion of the vinylic groups of the copolymer remain saturated by the modifier group substituents, the proportion of saturated vinylic groups controlling the extent of conjugation in the copolymer, thereby spatially modulating the semiconductor bandgap of the copolymer.

35. A method as claimed in claim 34, wherein the poly(arylene-1,2-ethanediyl) precursor polymer comprises a homopolymer.

36. A method is claimed in claim 35, wherein the homopolymer comprises a poly(paraphenylene-1,2-ethanediyl) polymer, a poly(2,5 dimethoxy para phenylene-1,2-ethanediyl) polymer, a poly(thienylene-1,2-ethanediyl) polymer, a poly(2,5 dimethyl-para-phenylene-1,2-ethanediyl)polymer, a poly(2-methoxy-5-(2'-methylpentyloxy)-para phenylene-1,2-ethanediyl)polymer or a poly(2-methoxy-5-(2'-ethylhexyloxy)-para-phenylene-1,2-ethanediyl) polymer.

37. A method as claimed in any one of claims 34 to 36, wherein the heating is performed substantially in the absence of acid.

38. A method as claimed in any one of claims 34 to 37, wherein the temperature of heating is in the range 200 to 300°C.

39. A method as claimed in any one of claims 34 to 38, wherein the heating time is up to 12 hours.

40. A method of manufacturing a semiconductive copolymer comprising:

(a) reacting a quantity of a first monomer with a quantity of a second monomer in a solvent comprising a mixture of water and an alcohol;

(b) separating the reaction product therefrom;

(c) dissolving the reaction product in an alcohol the same as or different from said first mentioned alcohol;

(d) forming from the result of step (c) a conjugated polymer film, the quantities in step (a) being selected so that in the conjugated copolymer the semiconductor bandgap is controlled so as to control the optical properties of the copolymer.

41. A method as claimed in claim 40, wherein the semiconductor bandgap has been spatially modulated so as to increase the quantum efficiency of the copolymer when excited to luminesce.

42. A method as claimed in claim 40 or claim 41, wherein the semiconductor bandgap has been spatially modulated so as to select the wavelength of radiation emitted during luminescence.

43. A method as claimed in any one of claims 40 to 42, wherein the semiconductor bandgap has been spatially modulated so as to select the refractive index of the copolymer.

44. A copolymer obtainable from the method of claim 33.

45. A copolymer as claimed in claim 44, wherein the para-phenylene constitutes an amount in the range 85-95% and wherein the second component is 2,5 dimethoxy-para-phenylene.

46. A conjugated semiconductive copolymer obtainable from the method of claim 40 or claim 41, wherein the first monomer is present in the range 90-95% and forms p-phenylene vinylene units in the copolymer; and the second monomer is present in the range 5-10% and forms 2,5-dimethyl-phenylene vinylene, 2-methoxy-5-(2'-methylpentyloxy)-para-phenylene vinylene or 2-methoxy-5-(2'-ethylhexyloxy)-para-phenylene vinylene units in the copolymer.

47. A conjugated semiconductive copolymer comprising an amount of poly(p-phenylene vinylene) in the range 90 - 95%, and an amount of poly(2-methoxy-5-(2'-methylpentyloxy)-p-phenylene vinylene) in the range 5 to 10%.

48. A conjugated semiconductive copolymer comprising an amount of poly(p-phenylene vinylene) in the range 90 - 95%, and an amount of poly(2-methoxy-5-(2'-ethylhexyloxy)-p-phenylene vinylene) in the range 5 to 10%.

49. An electroluminescent device incorporating a conjugated poly(arylene vinylene) copolymer as claimed in any one of claims 1 to 19 or 44 to 48.

50. An electroluminescent device incorporating a conjugated poly(arylene vinylene) copolymer obtained by the method of any one of claims 20 to 43.

51. The use of a semiconductive conjugated copolymer comprising at least two chemically different monomer units which, when existing in their homopolymer forms, have different semiconductor bandgaps, the proportion of said at least two chemically different monomer units in the copolymer having been selected to modulate the semiconductor bandgap of the copolymer so as to control the optical properties of the copolymer in applications which depend on the luminescent properties of the said copolymer, the said copolymer having been formed in a manner to enable it to be laid down as a thin film without substantially affecting the luminescent characteristics of the copolymer, said copolymer being stable at operational temperature.

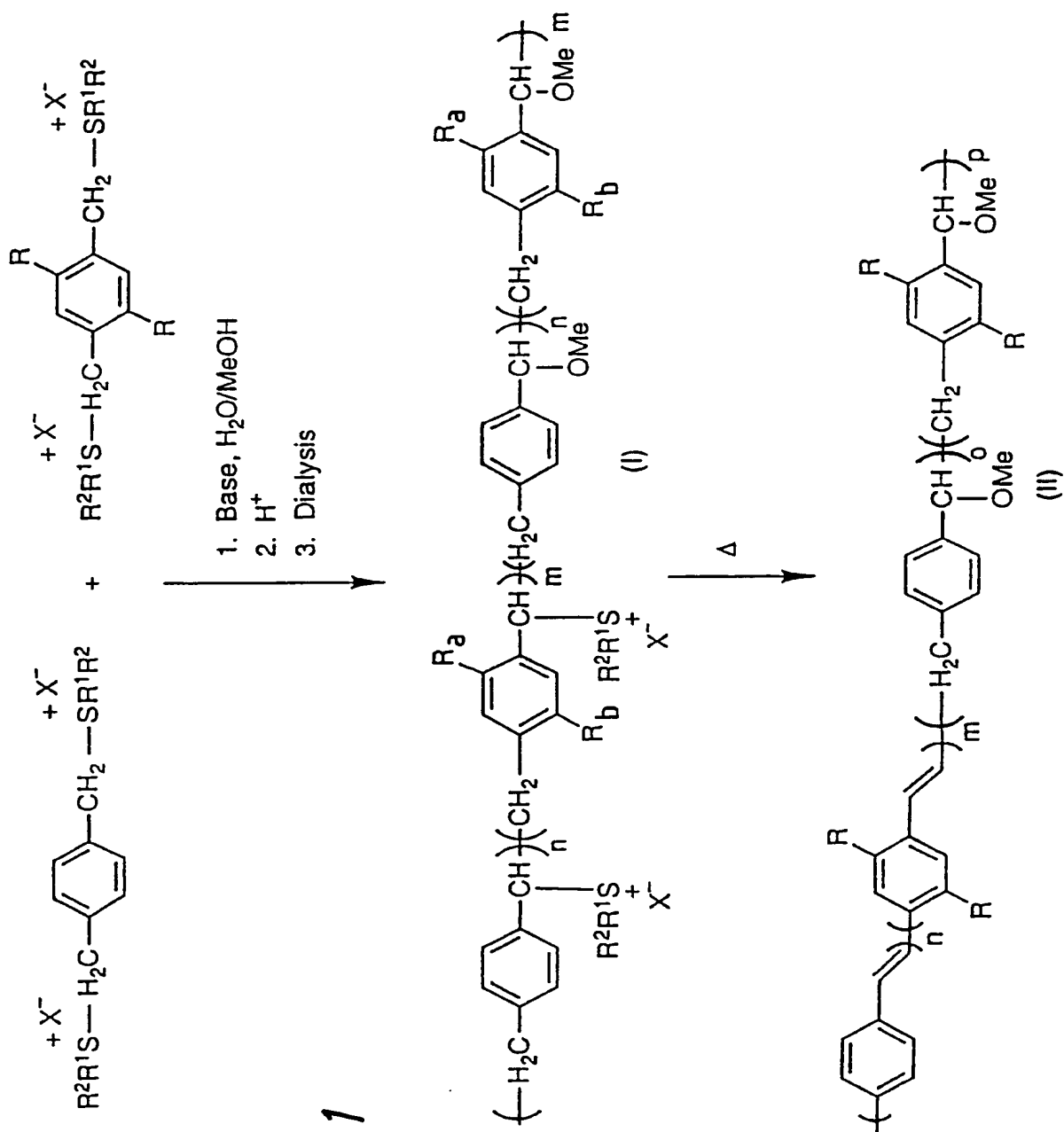


FIG. 1

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FIG. 2a

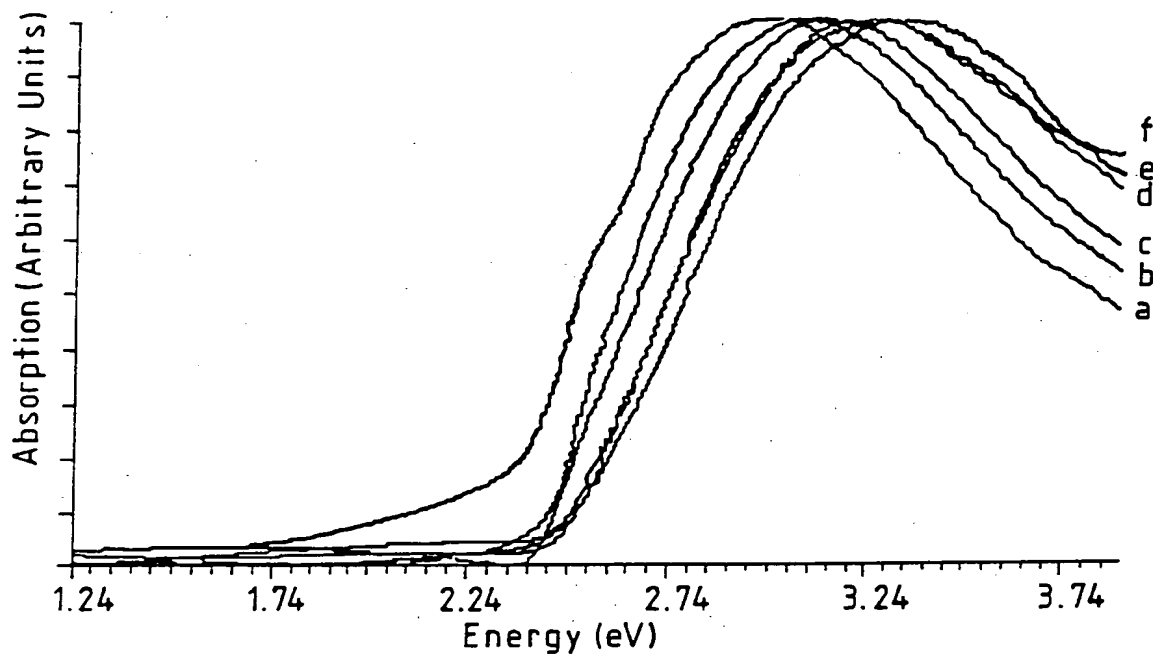
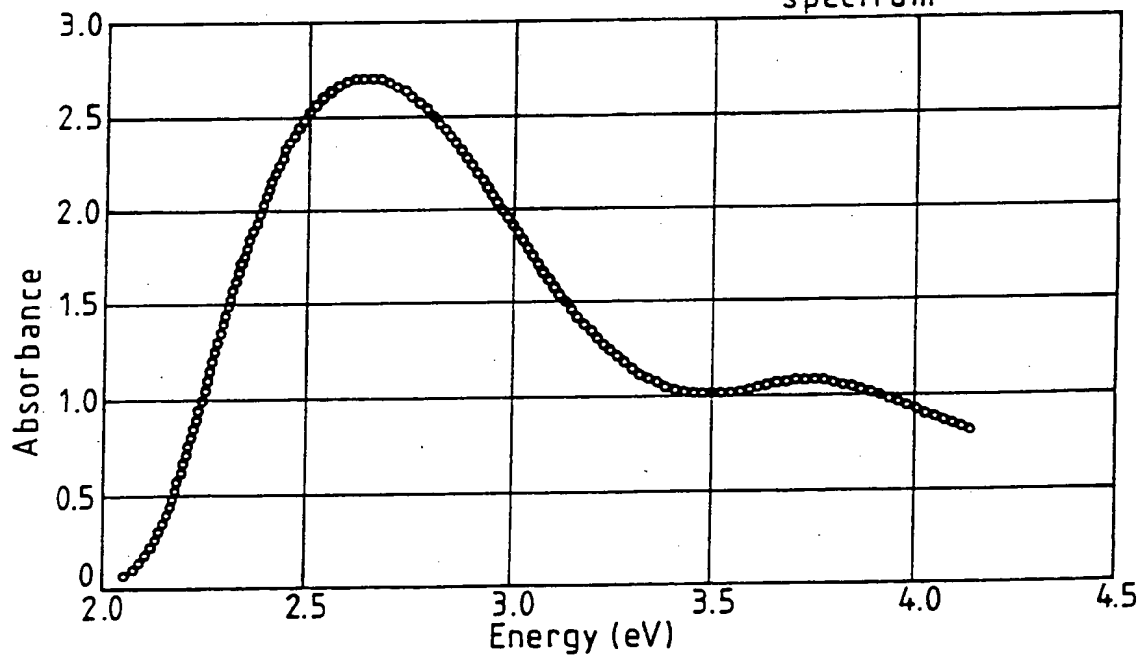


FIG. 2b PMPV absorption spectrum



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FIG. 3a

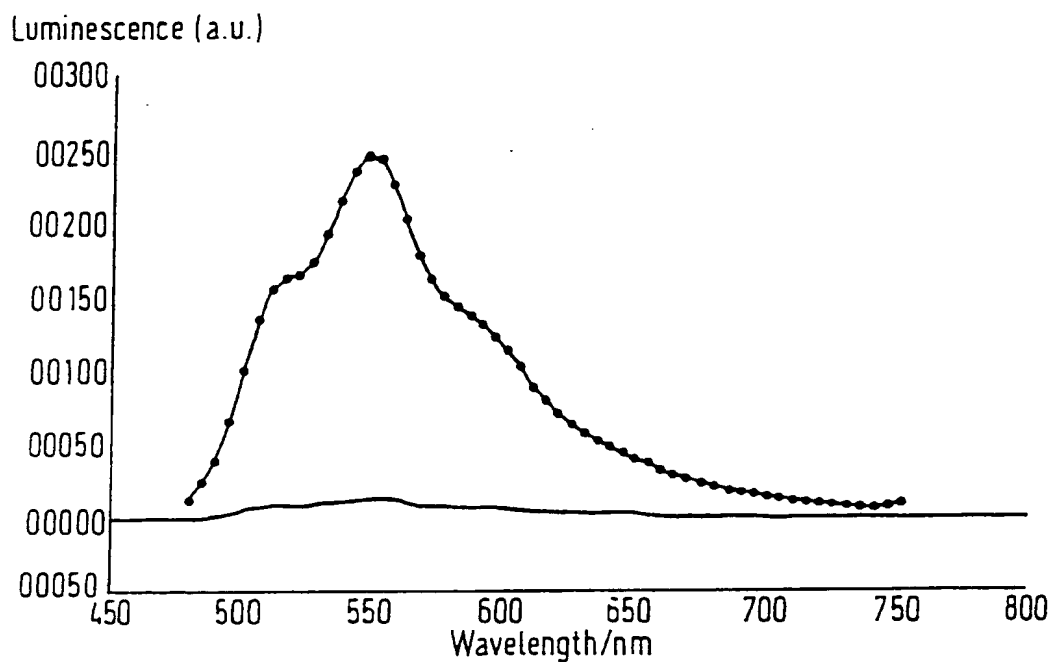
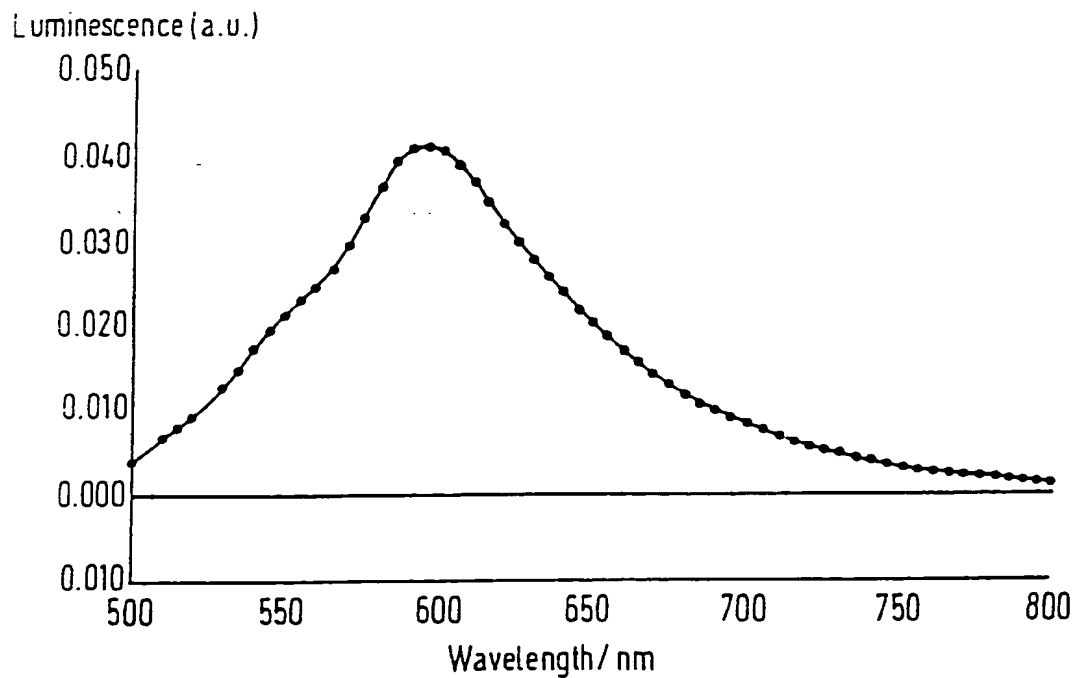


FIG. 3b





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FIG. 4a

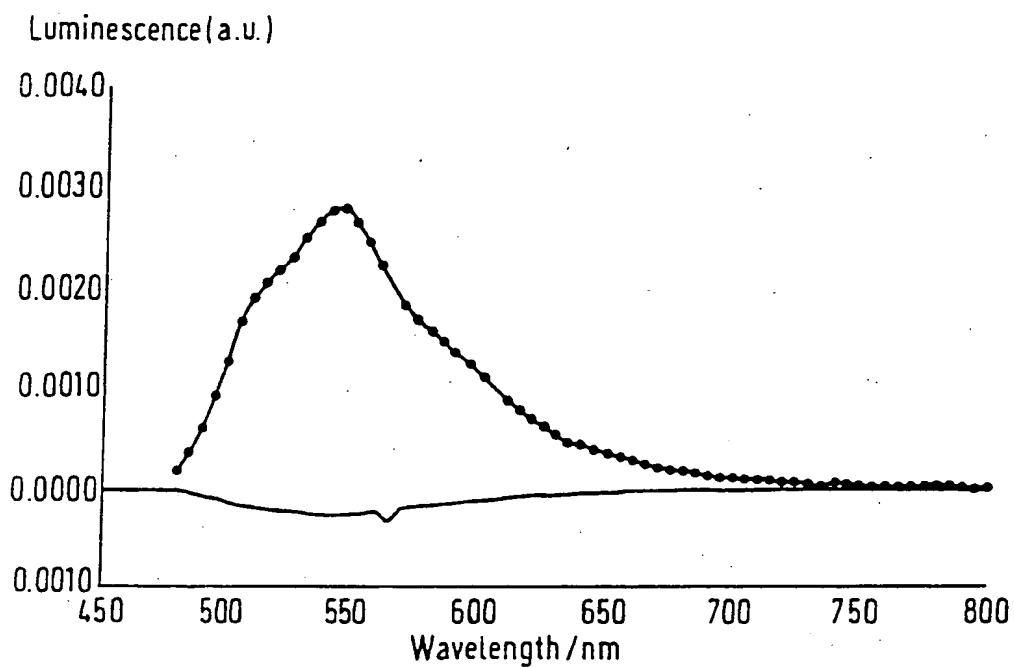
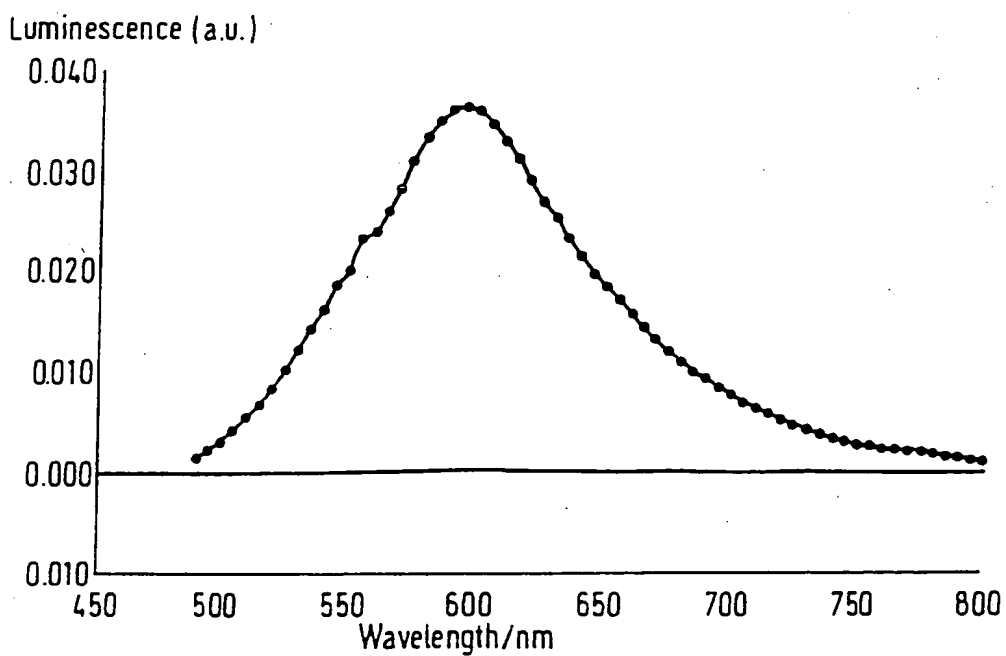
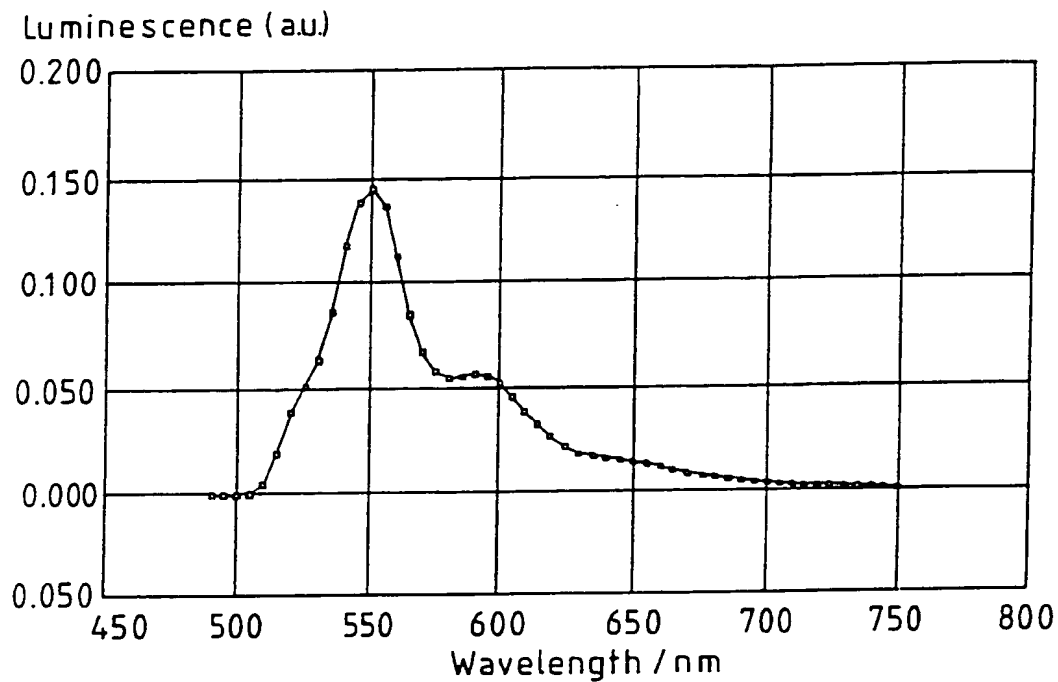
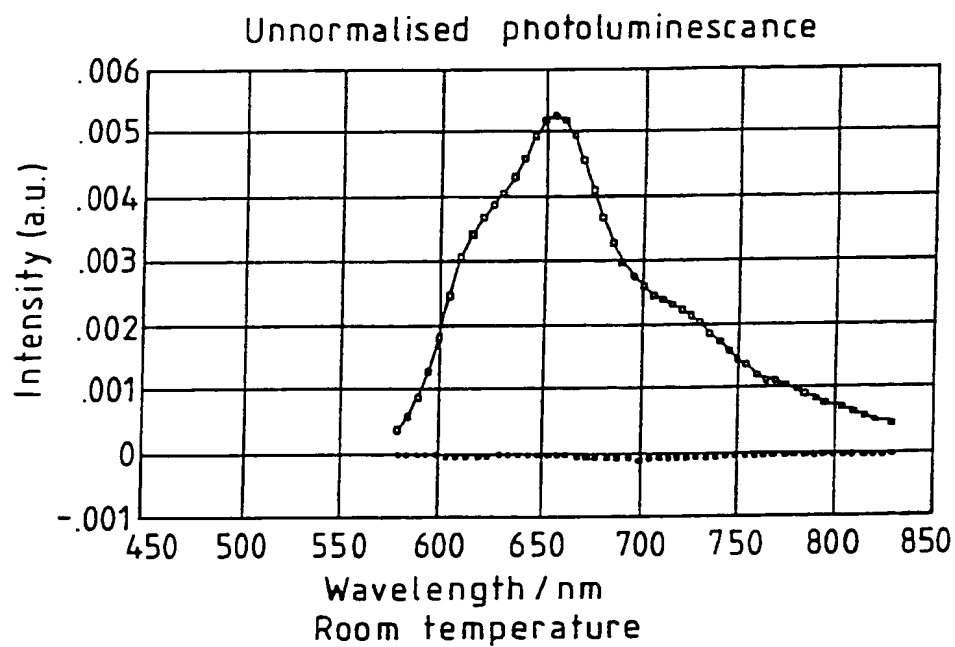


FIG. 4b



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*FIG. 5a**FIG. 5b*

210390 PMPV11

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FIG. 6

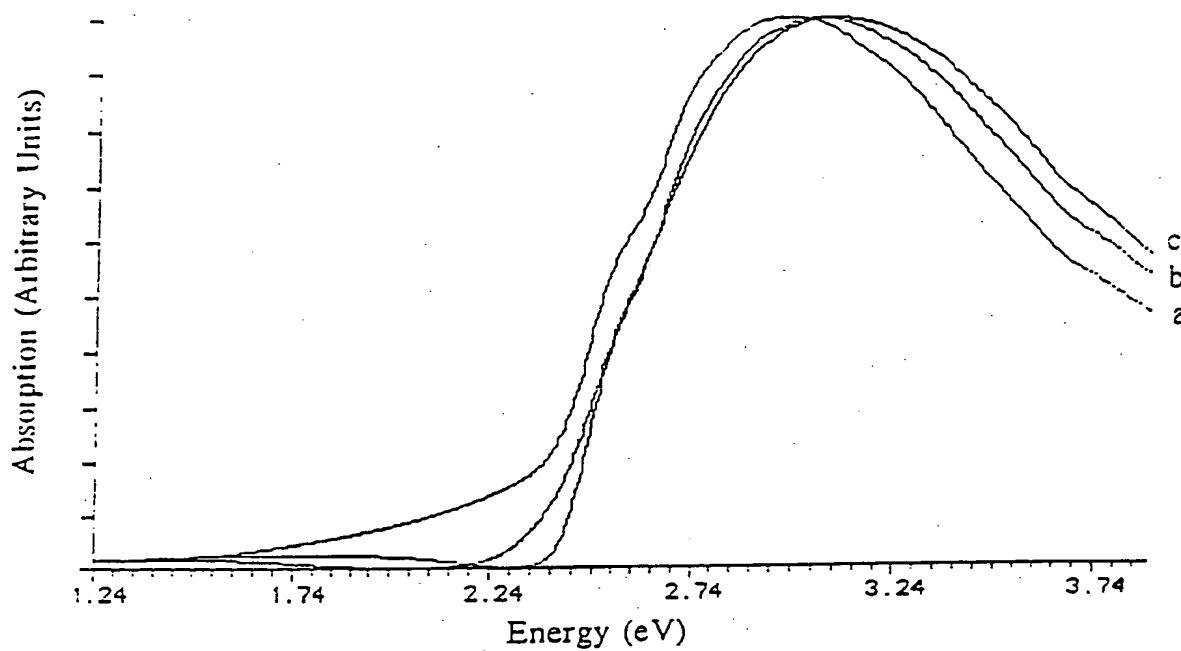
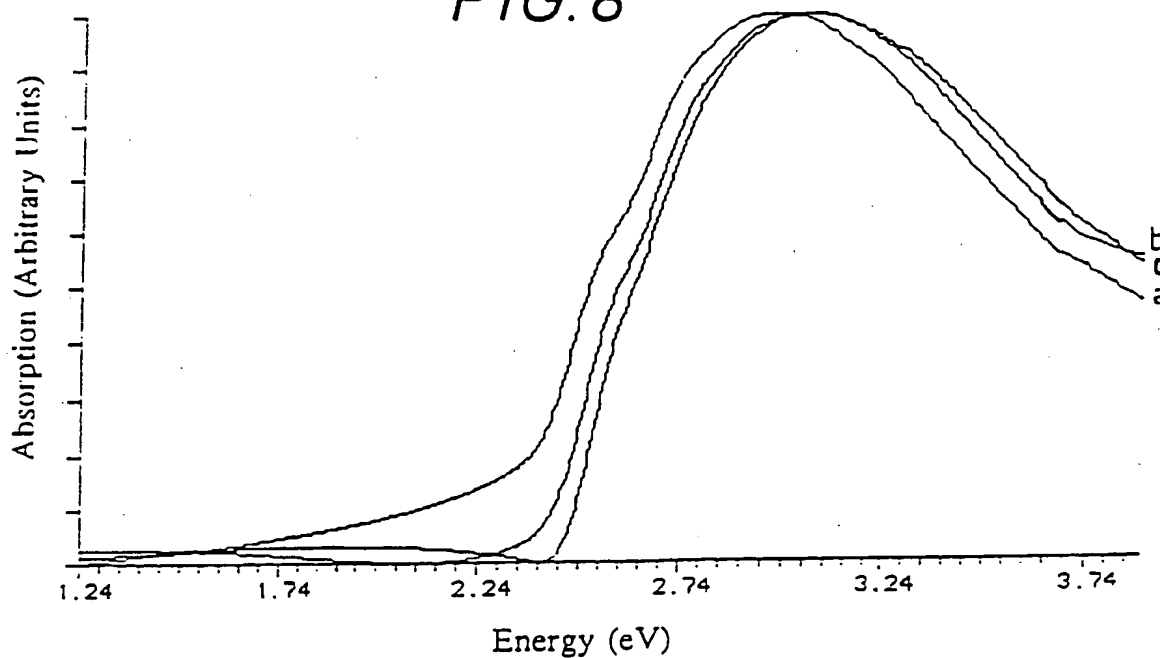
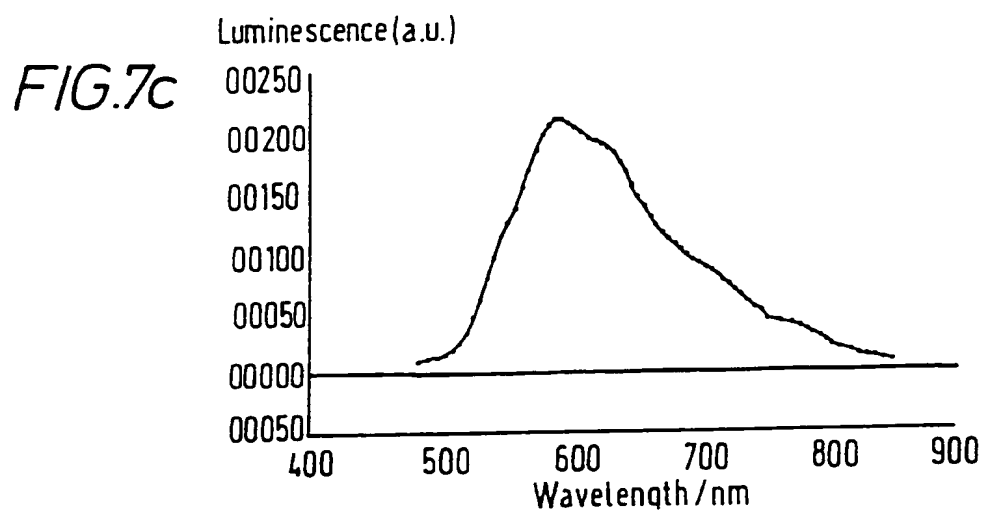
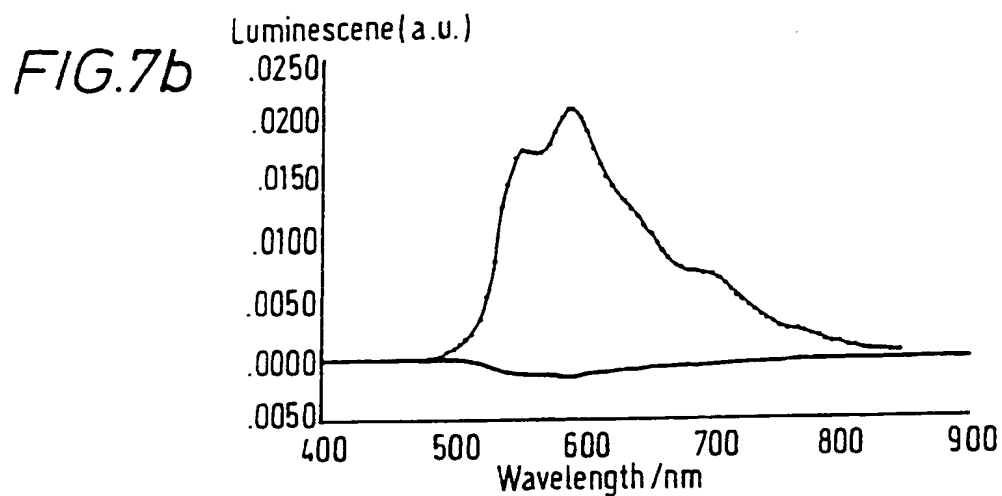
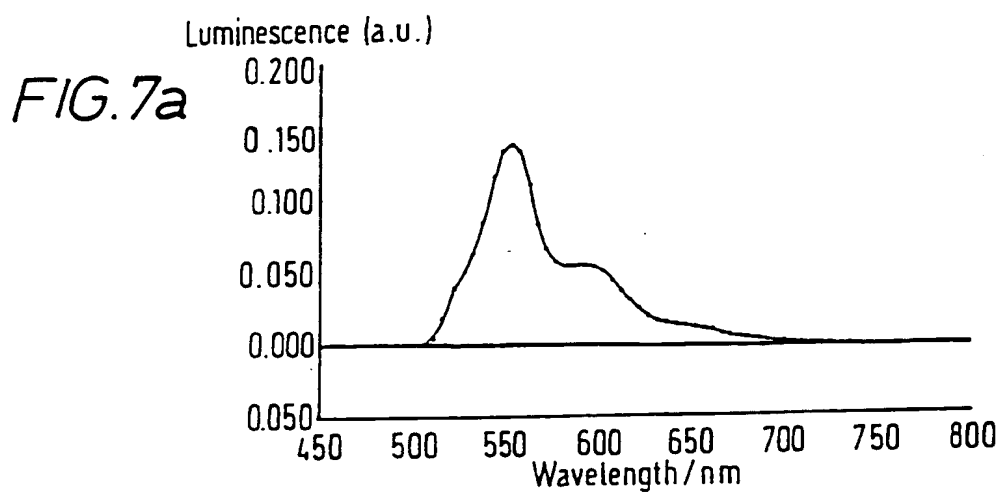


FIG. 8

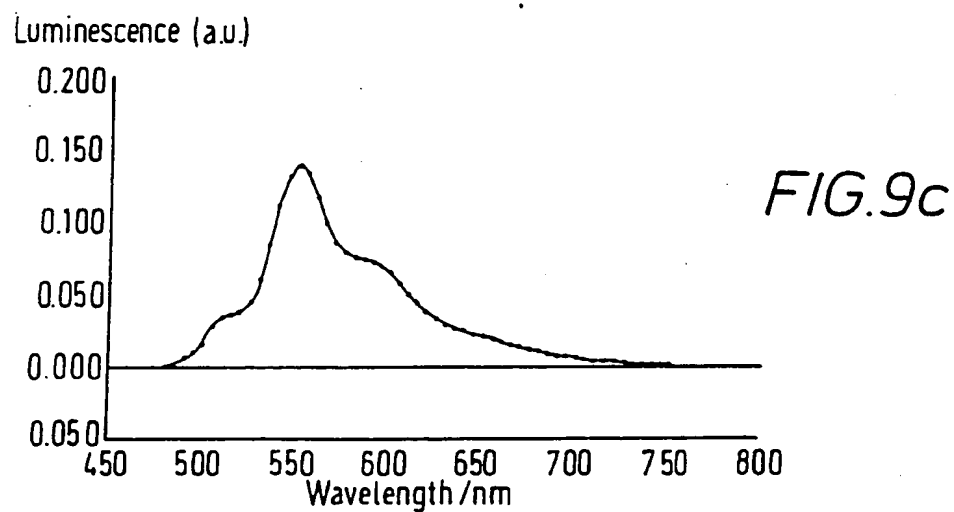
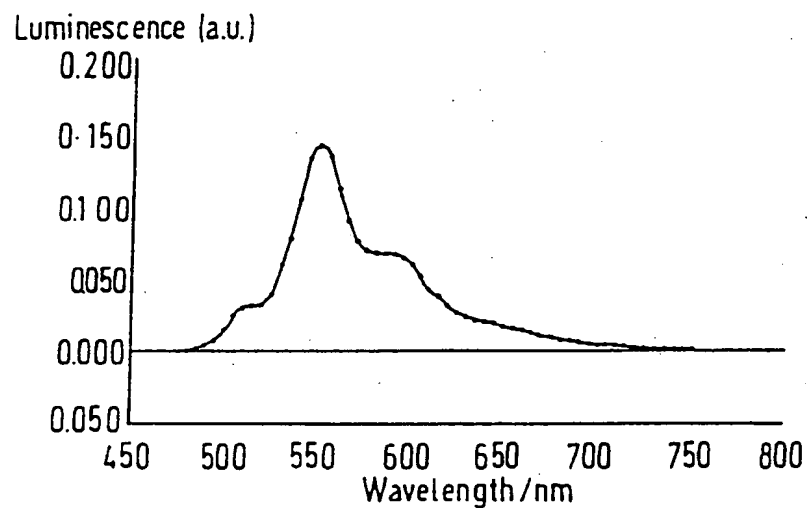
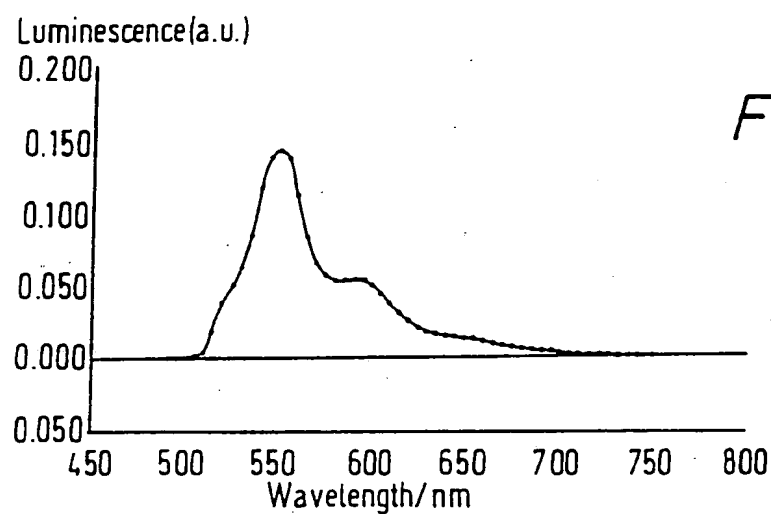


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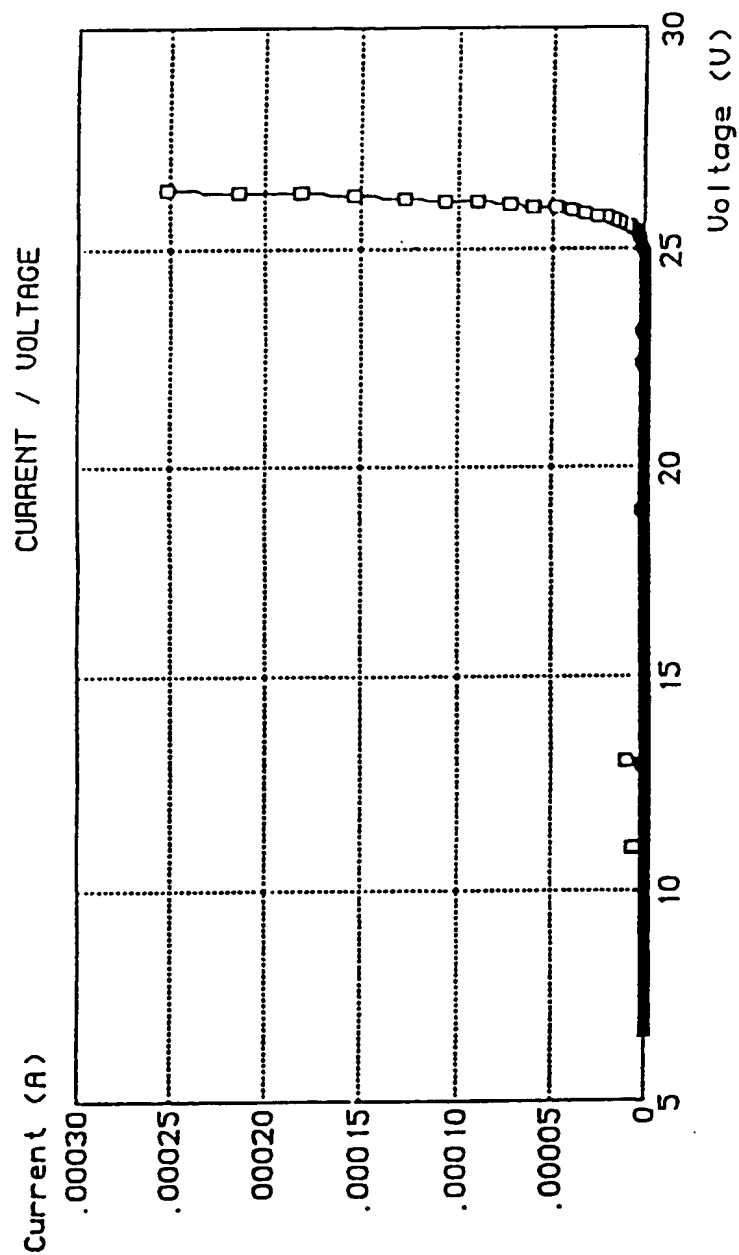
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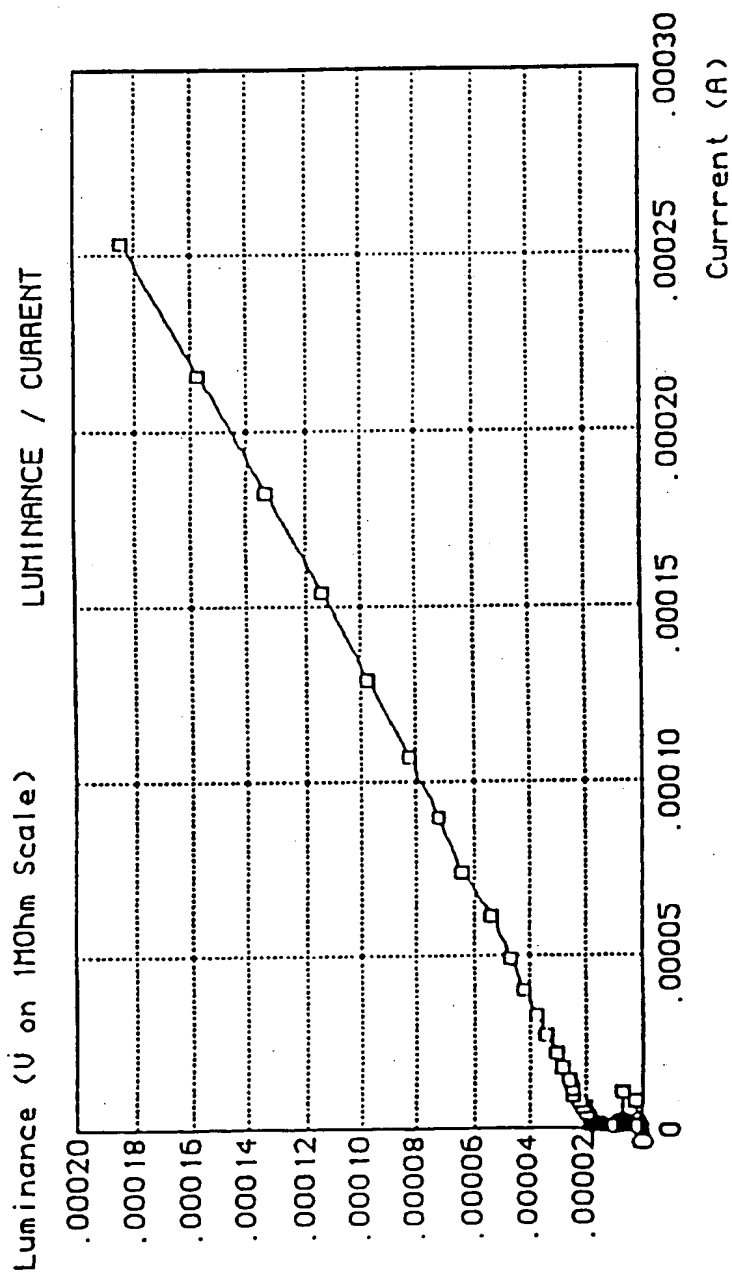
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FIG. 10a



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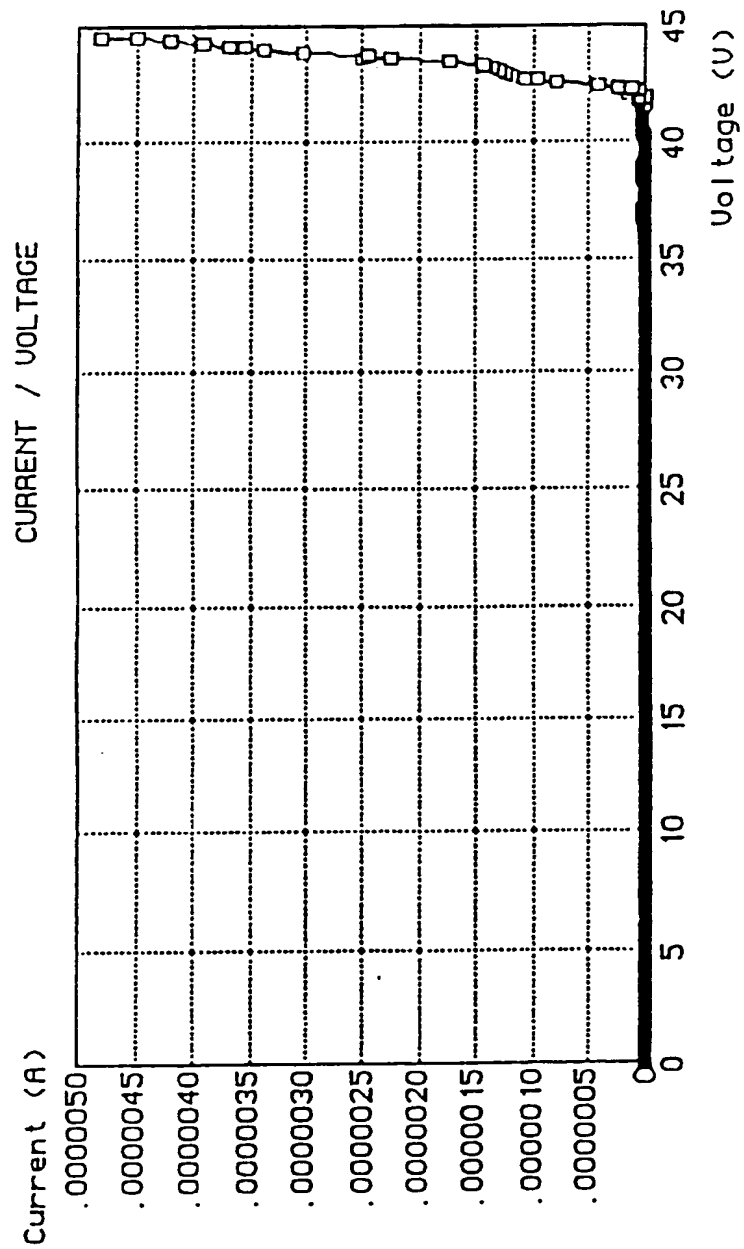
FIG. 10b



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FIG. 11a

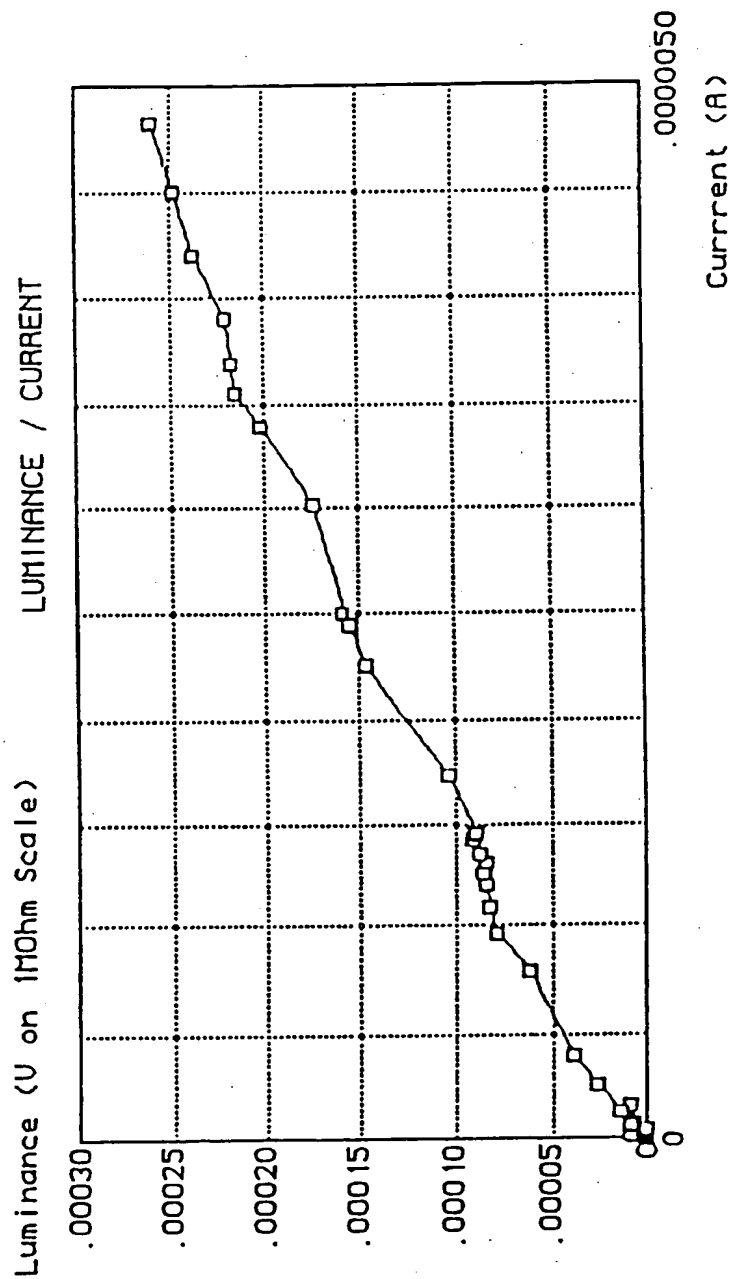


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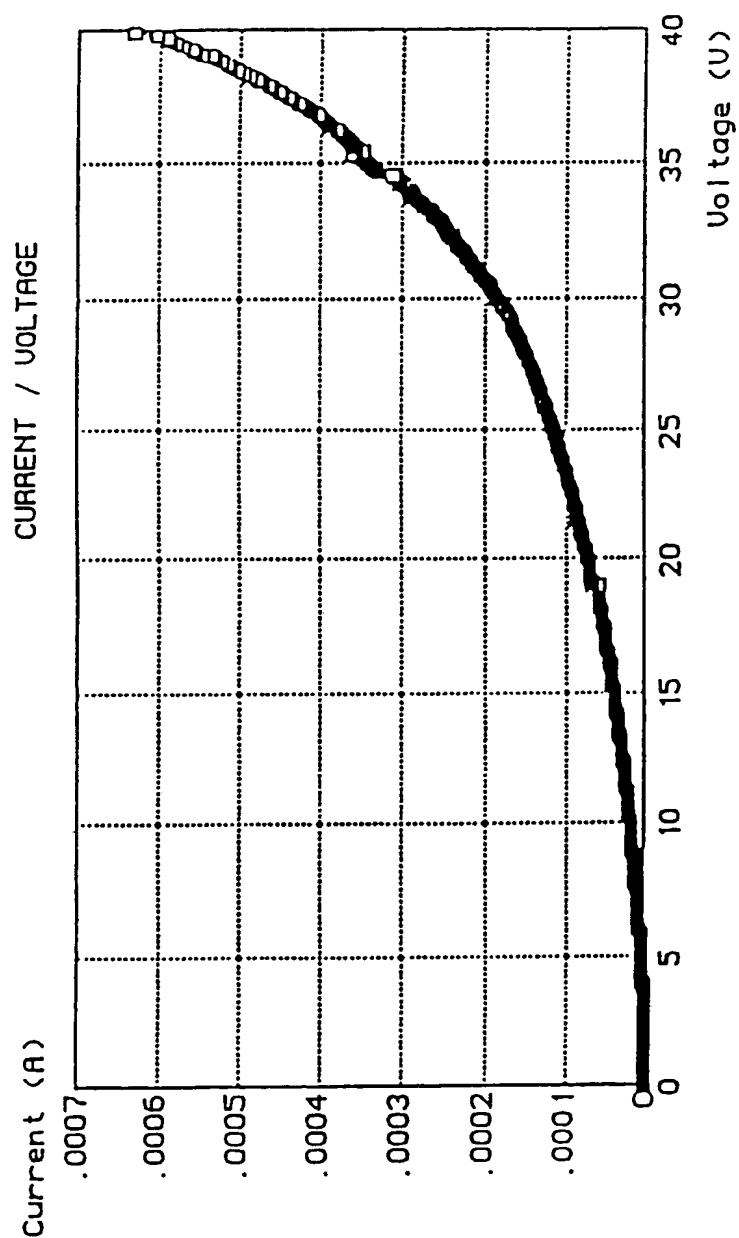
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FIG. 11b



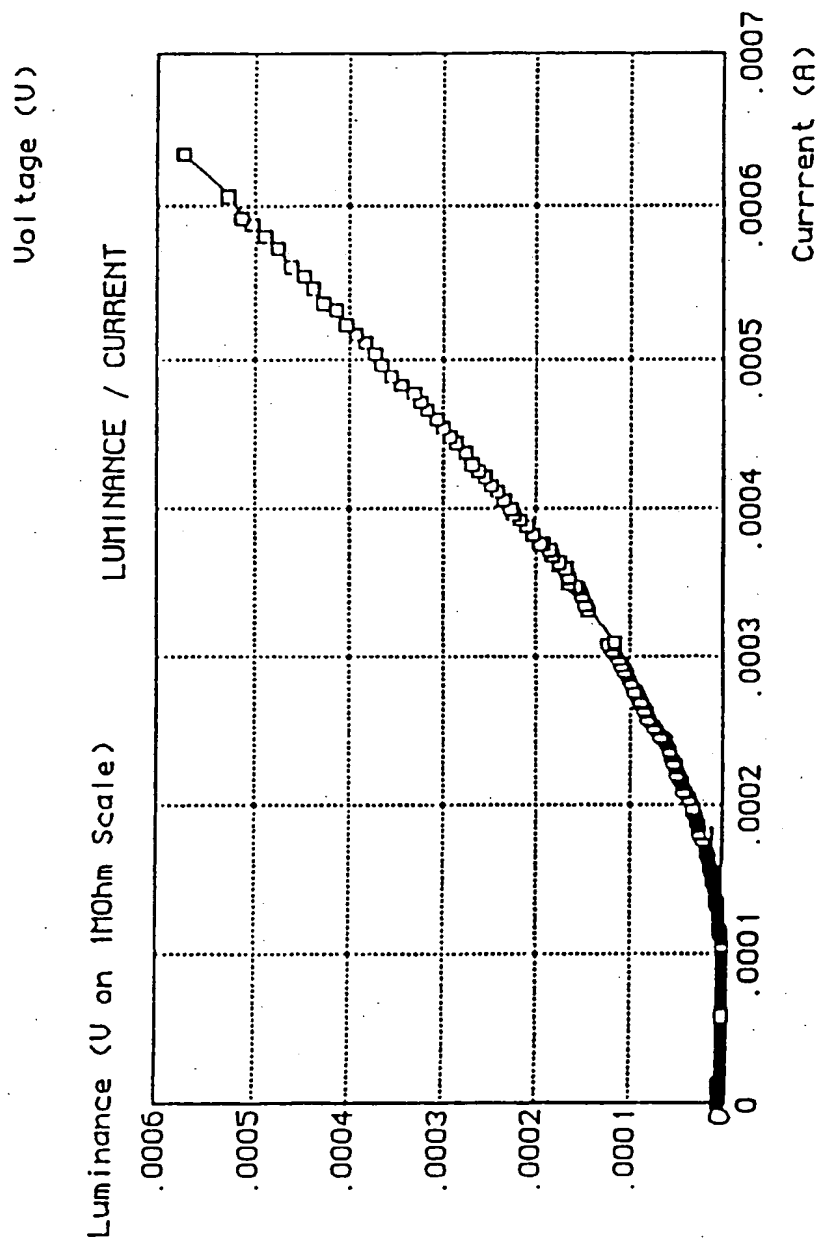
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FIG. 12a



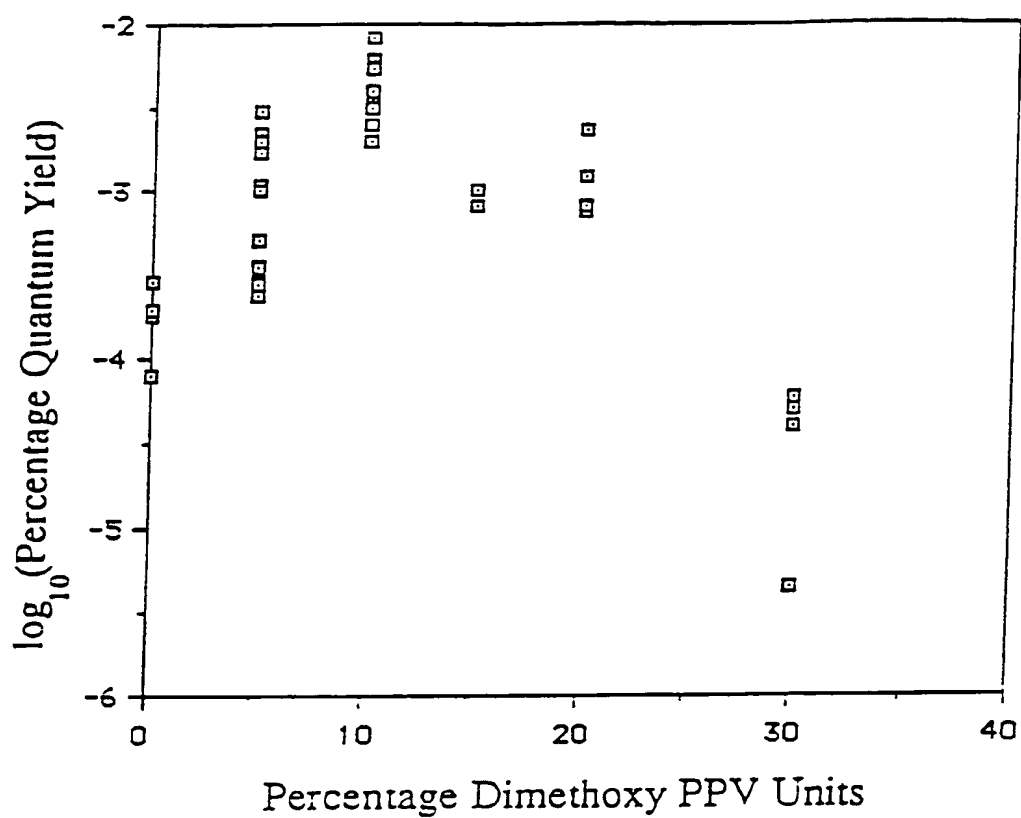
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FIG. 12b



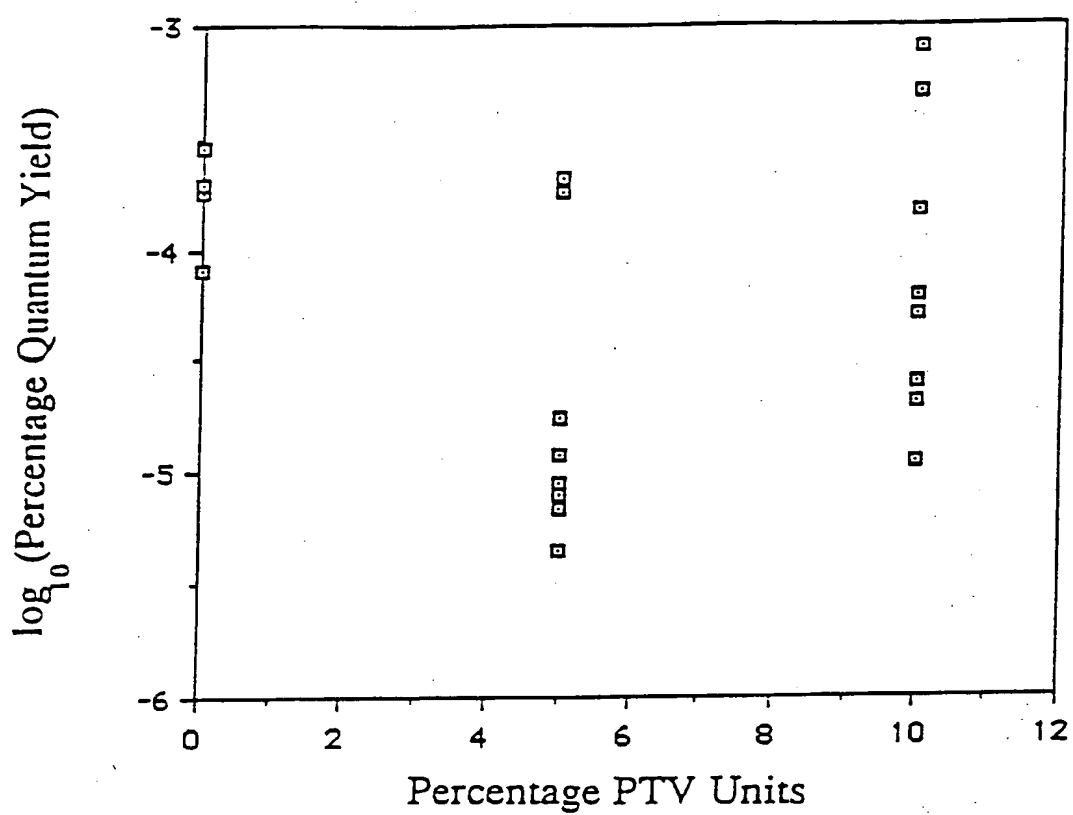
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FIG. 13



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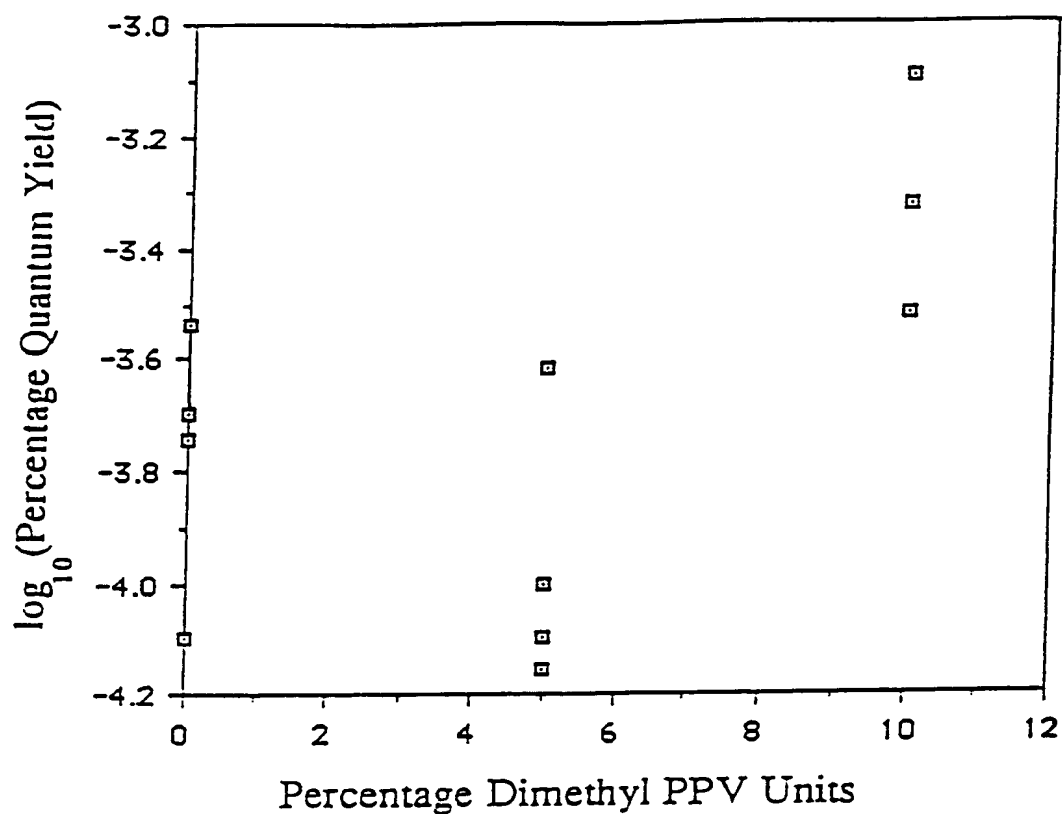
FIG. 14



Electroluminescent Quantum Yield of the Random Copolymers of PPV and PTV

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FIG. 15



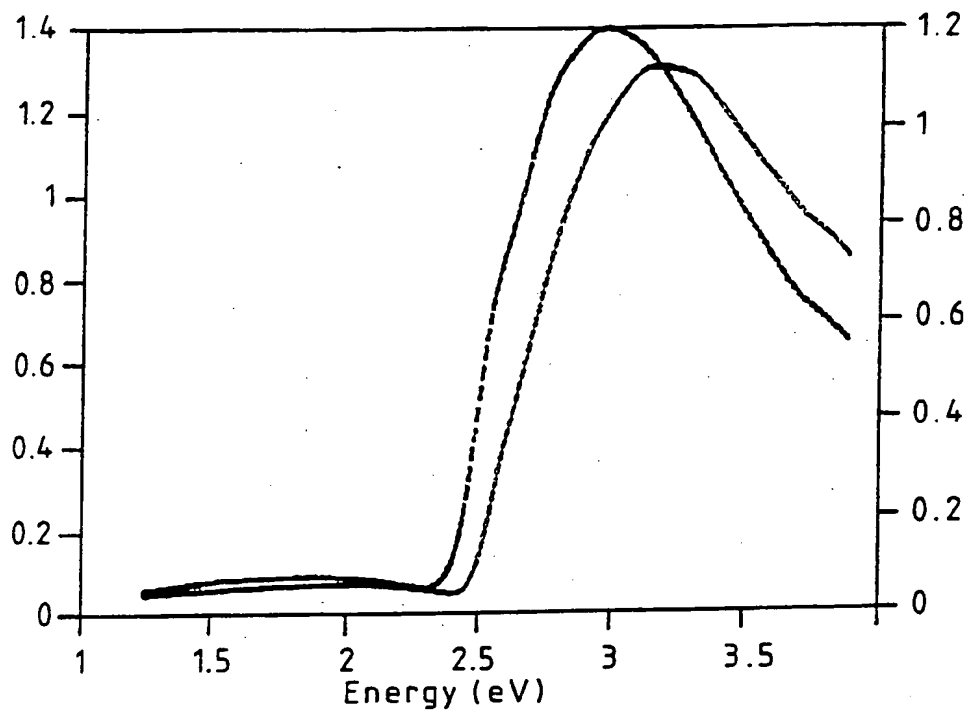
Electroluminescent Quantum Yield of the Random  
Copolymers of PPV and Dimethyl PPV

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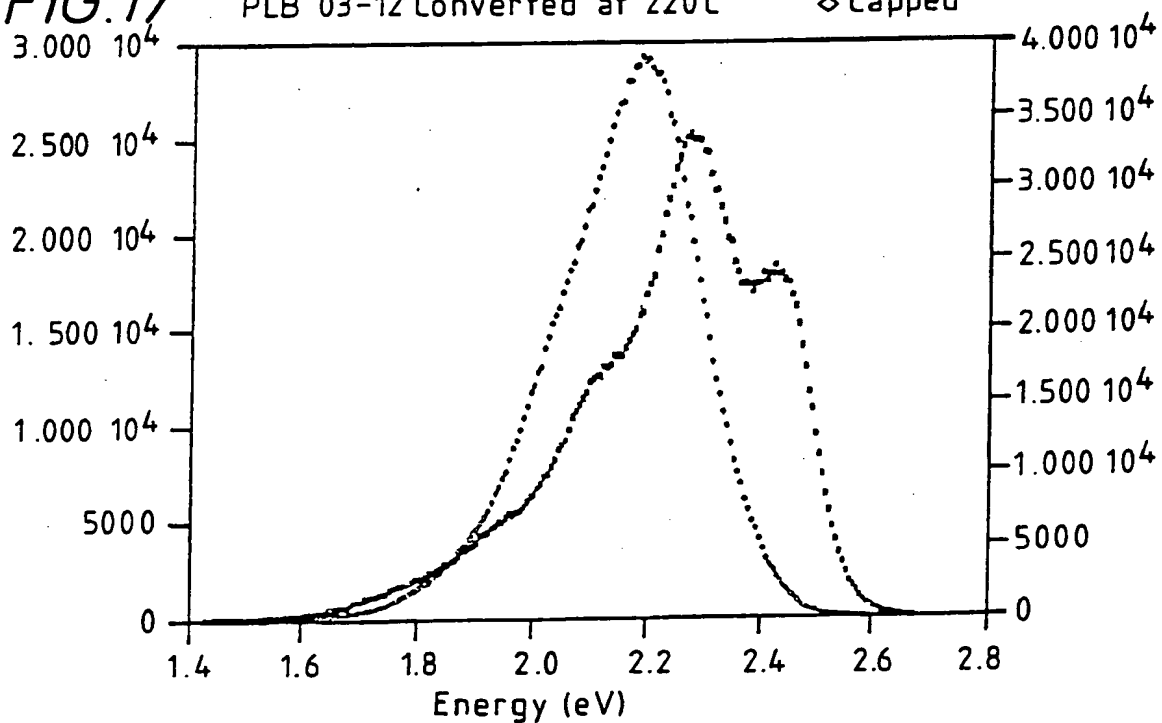
**FIG. 16**

□ Capped    ◇ Uncapped

PLB 03-12 Absorption Spectra

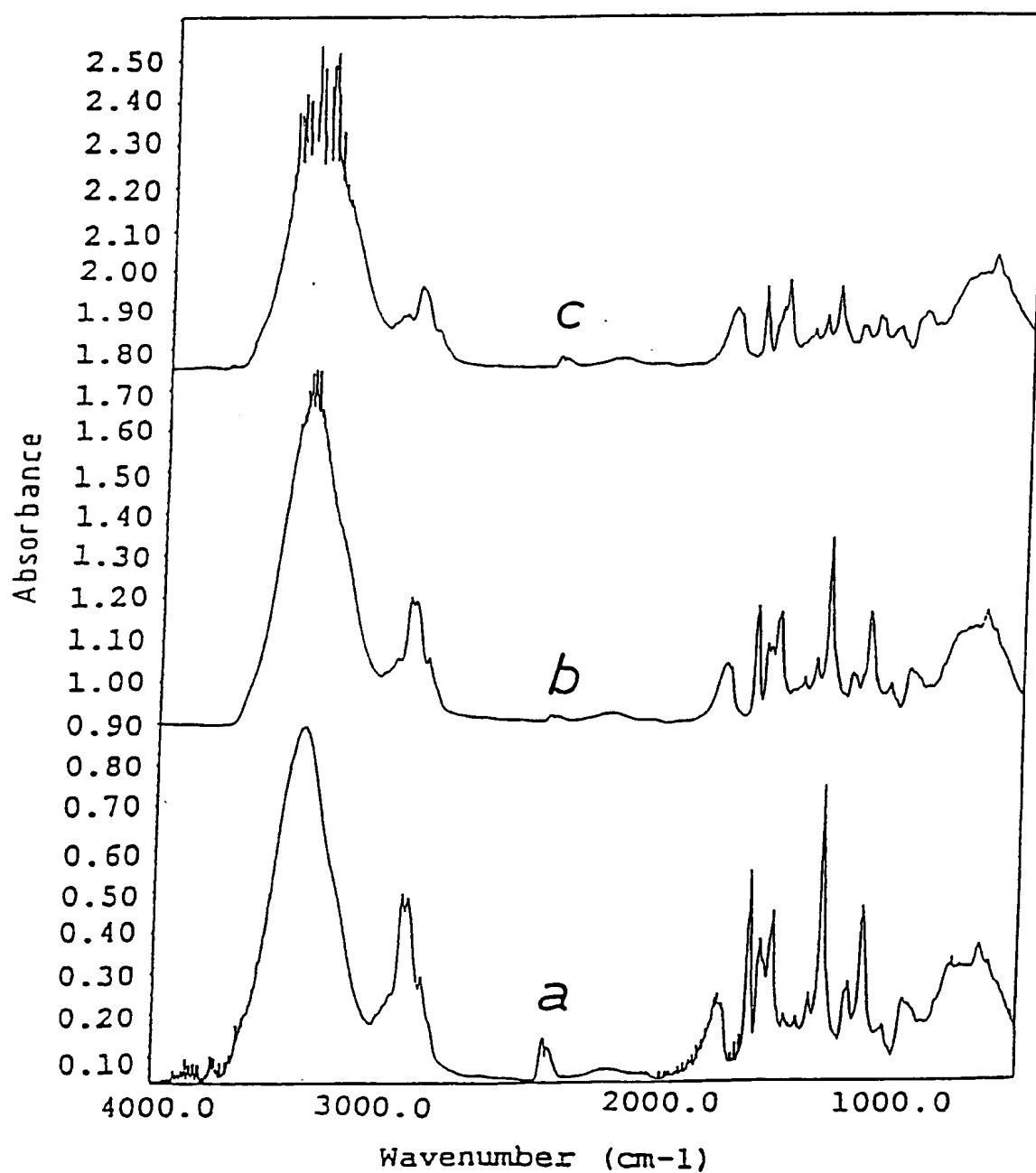
**FIG. 17**

PLB 03-12 Converted at 220°C

□ Uncapped  
◇ Capped**SUBSTITUTE SHEET**

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FIG. 18



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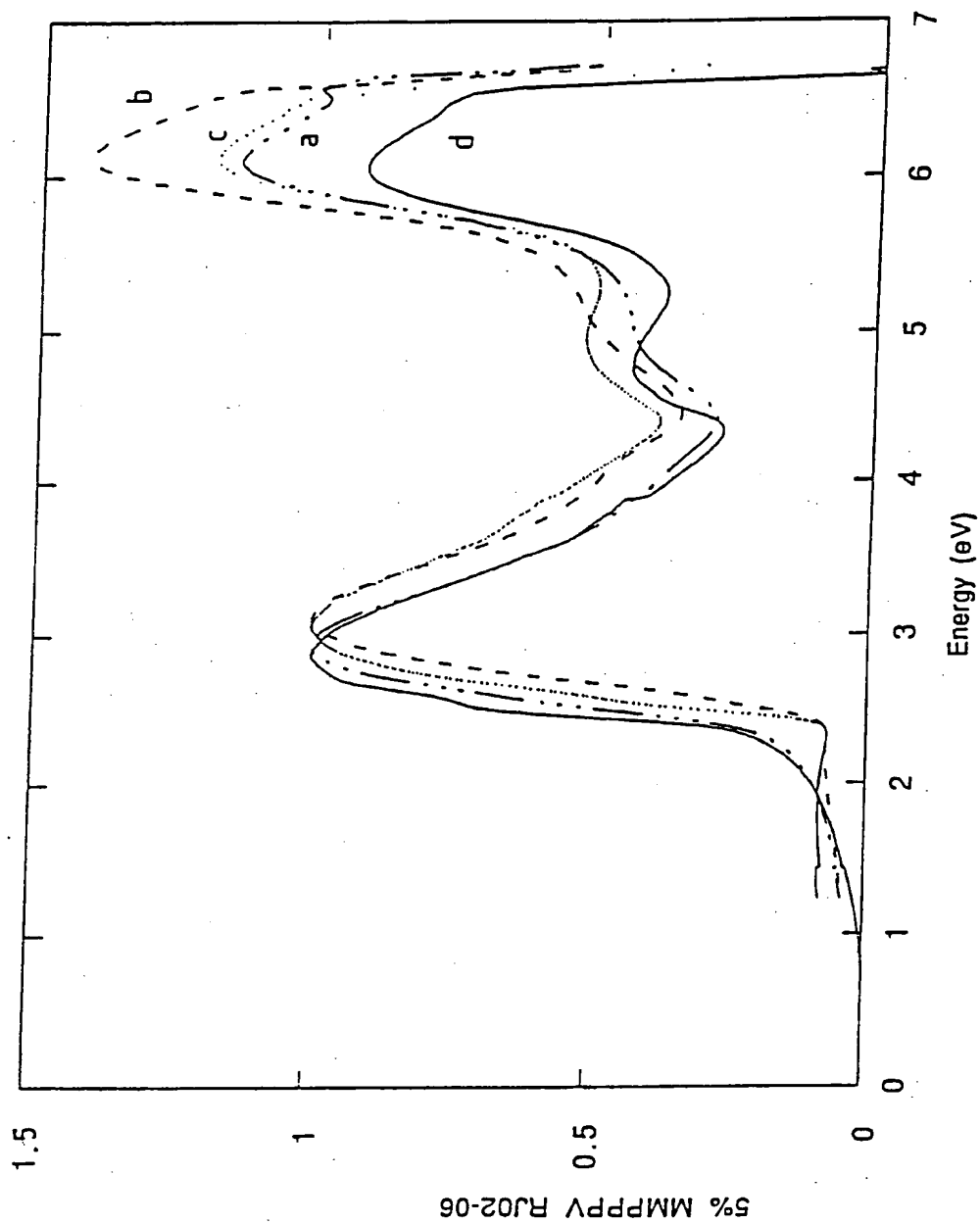
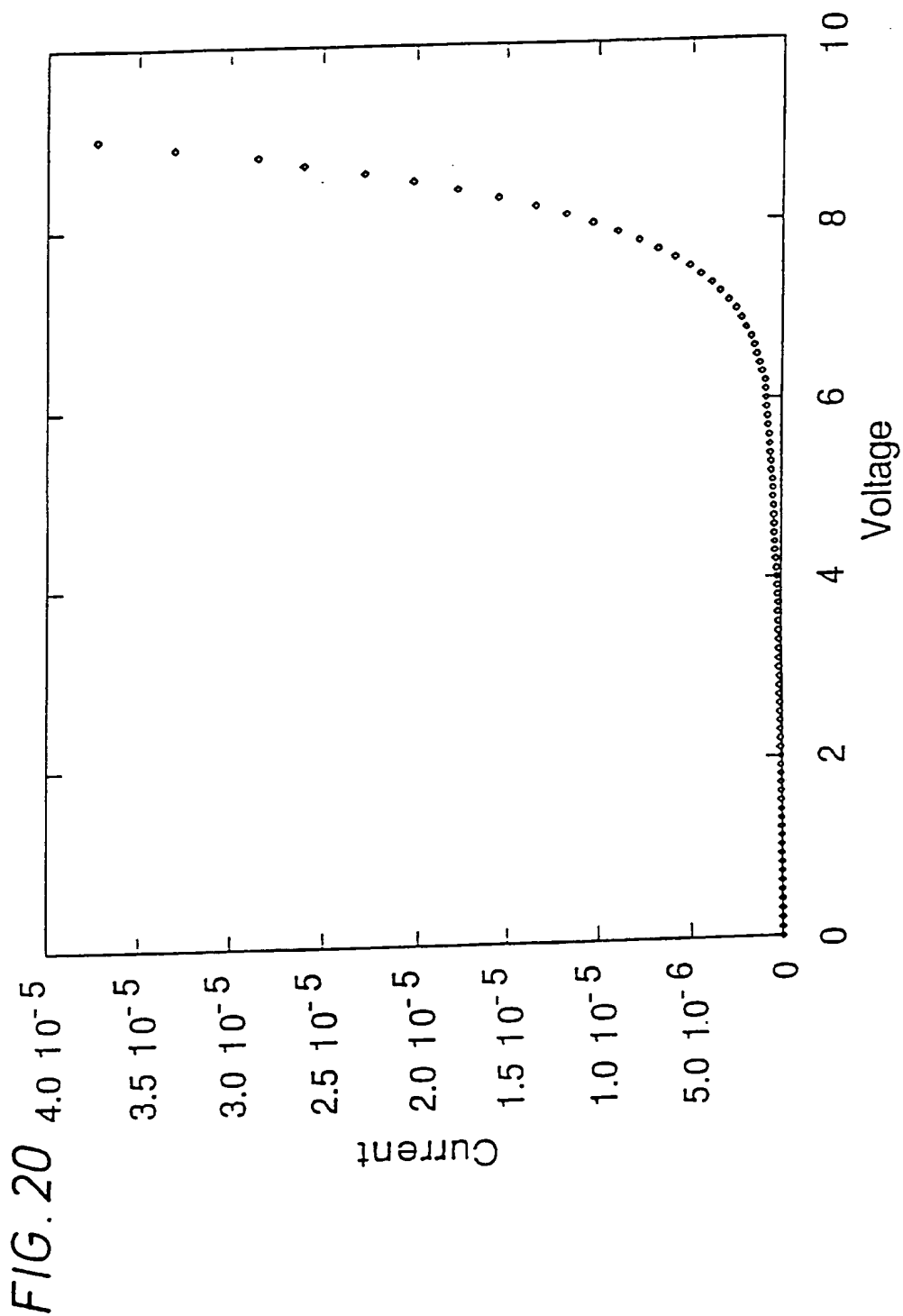


FIG. 19

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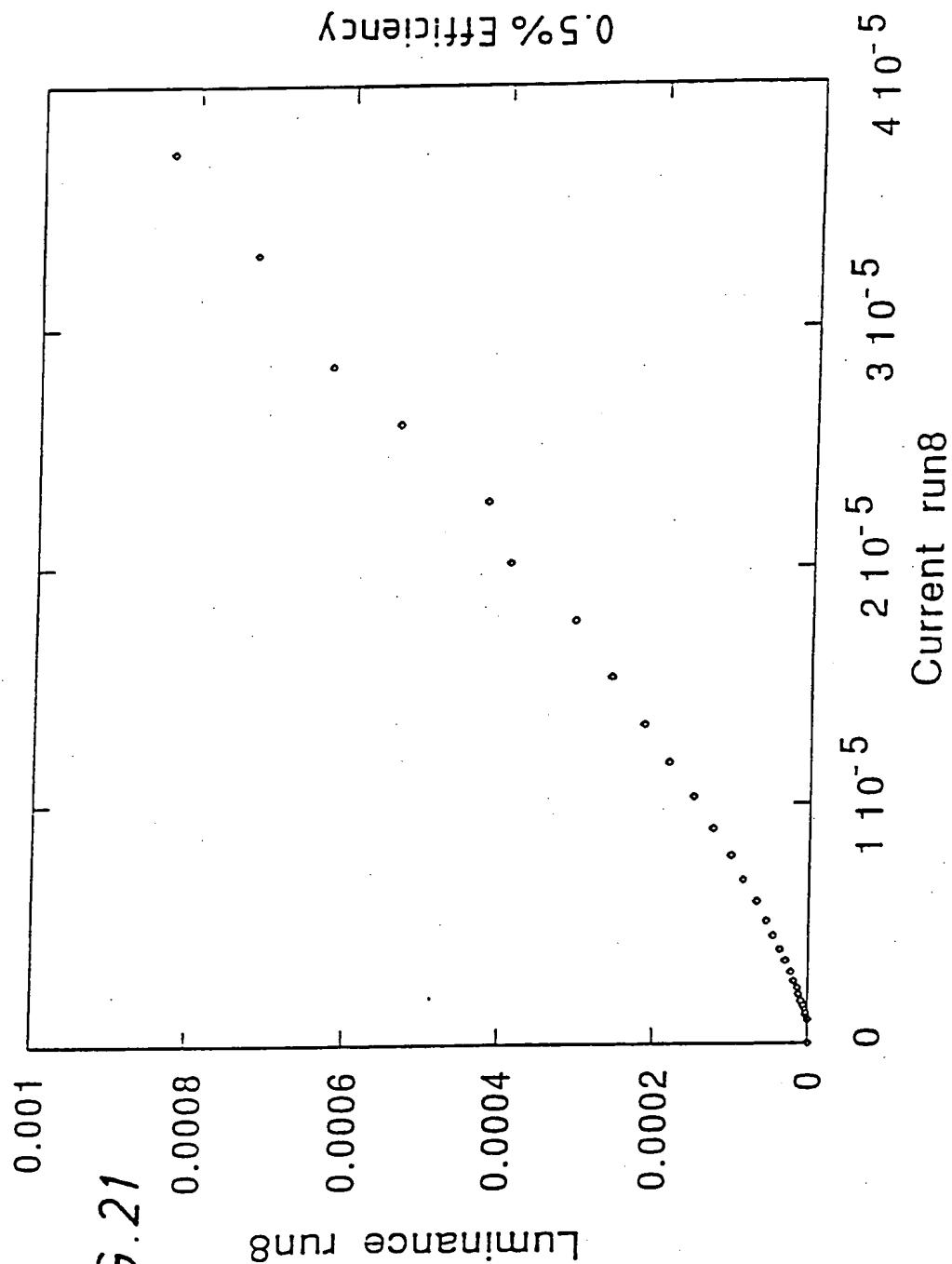
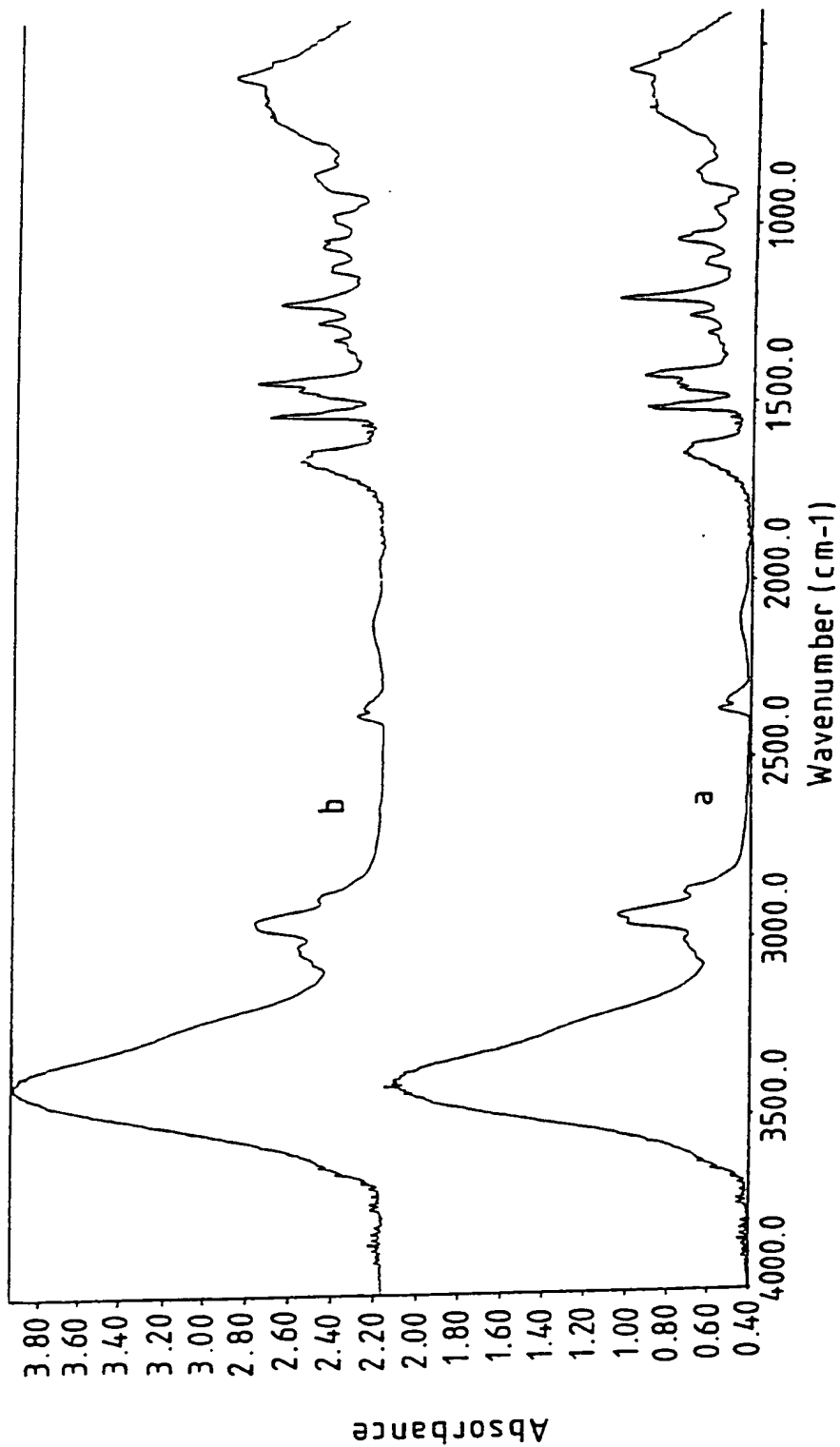


FIG. 21

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FIG. 22



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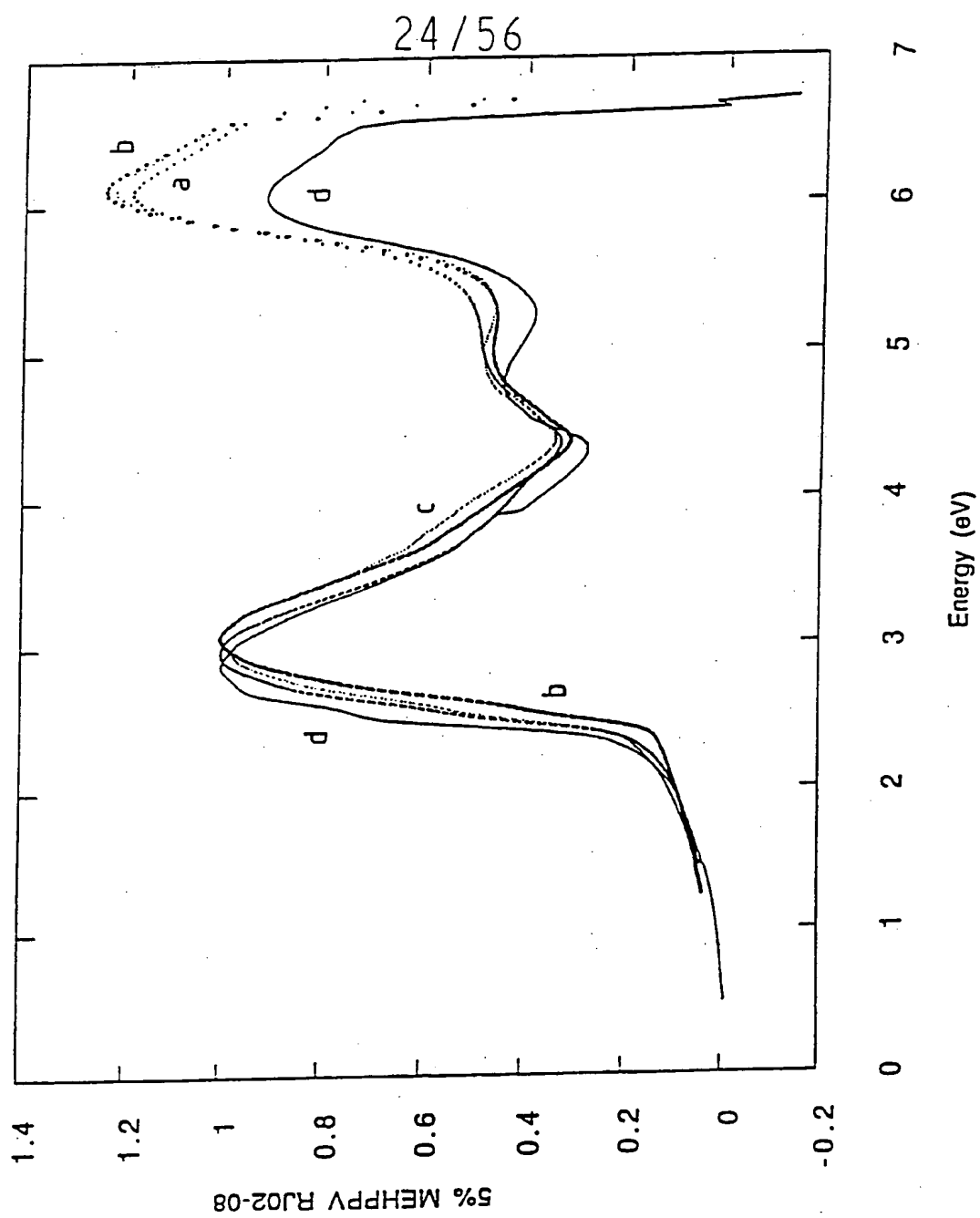
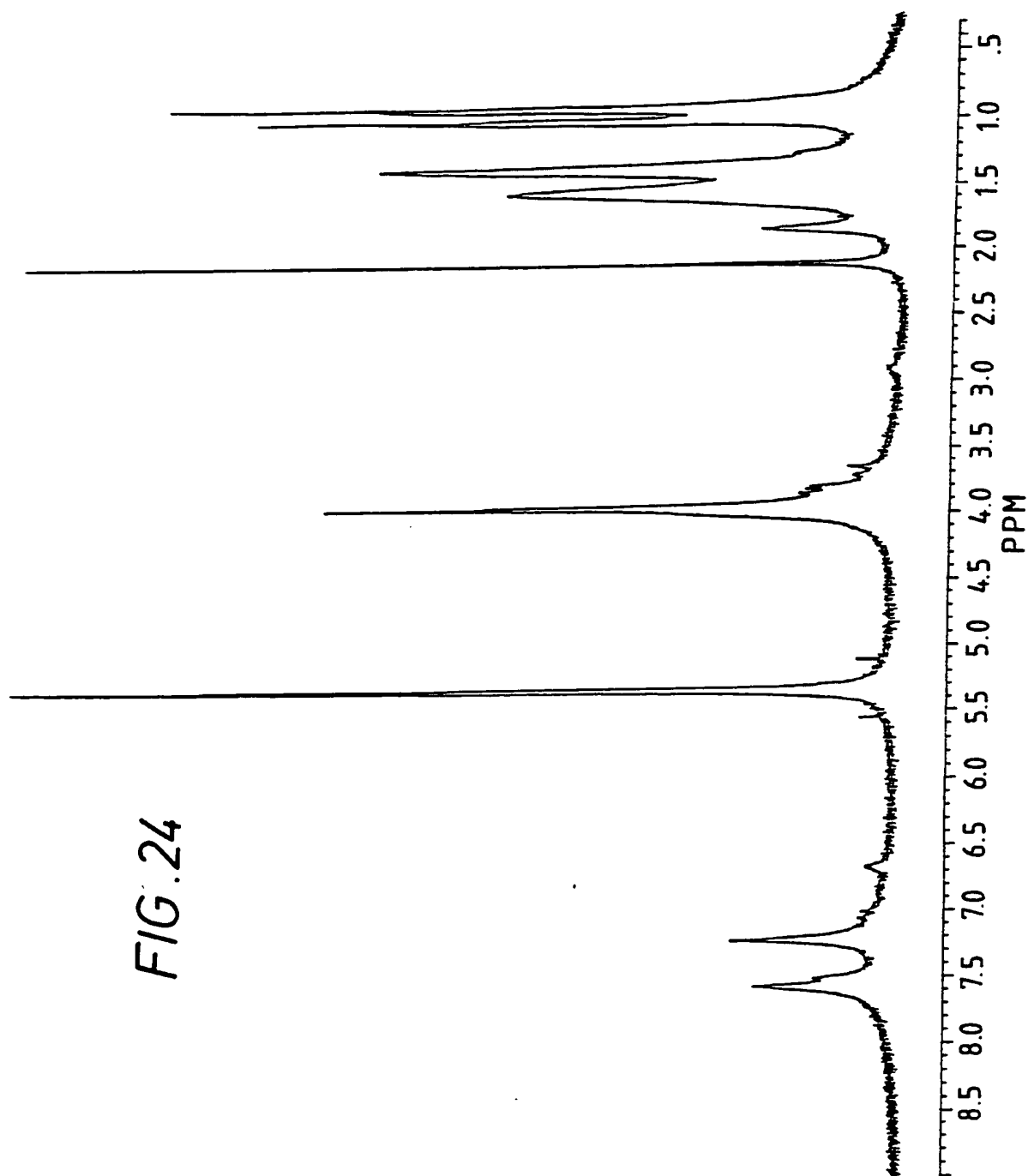


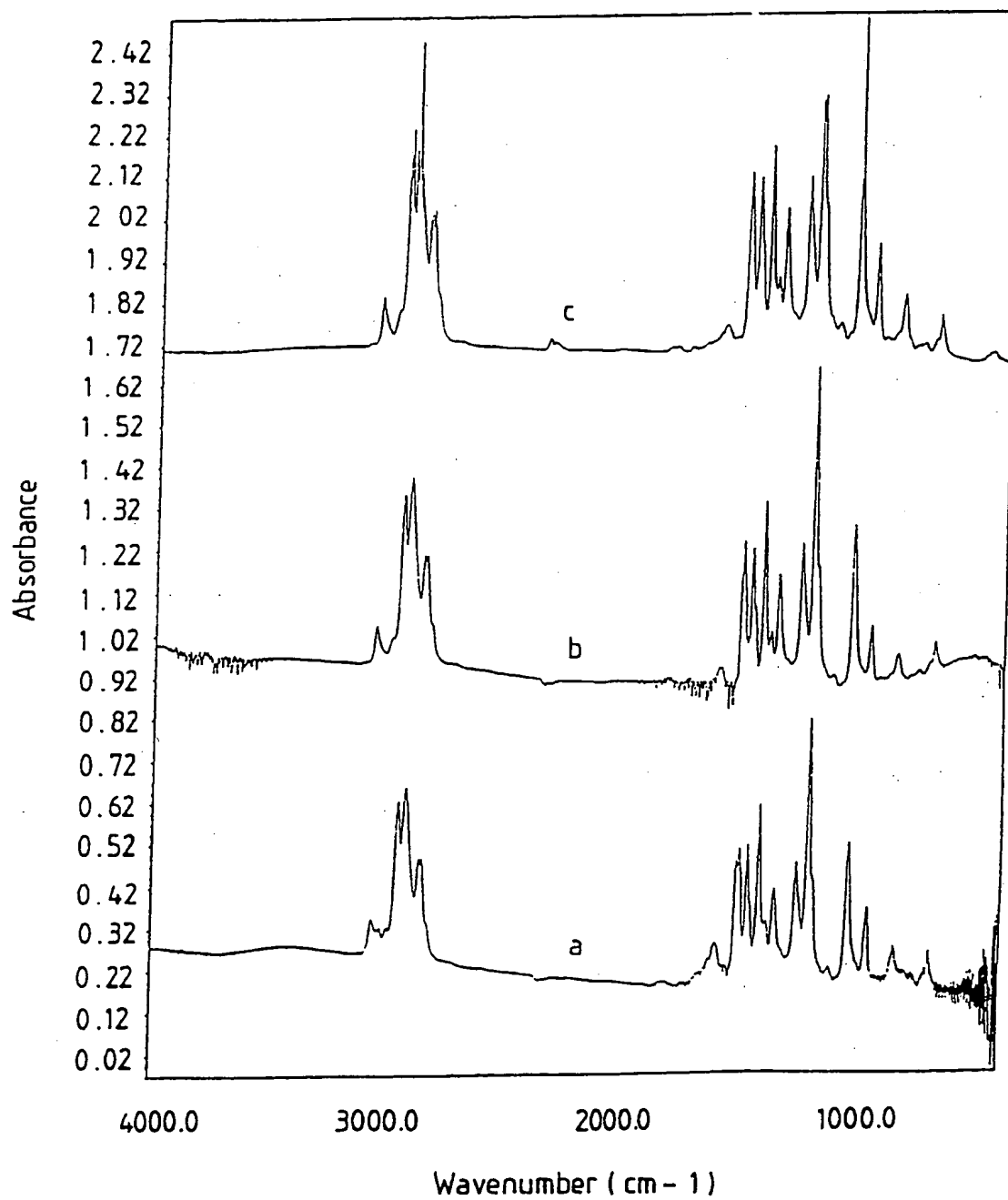
FIG. 23

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FIG. 25

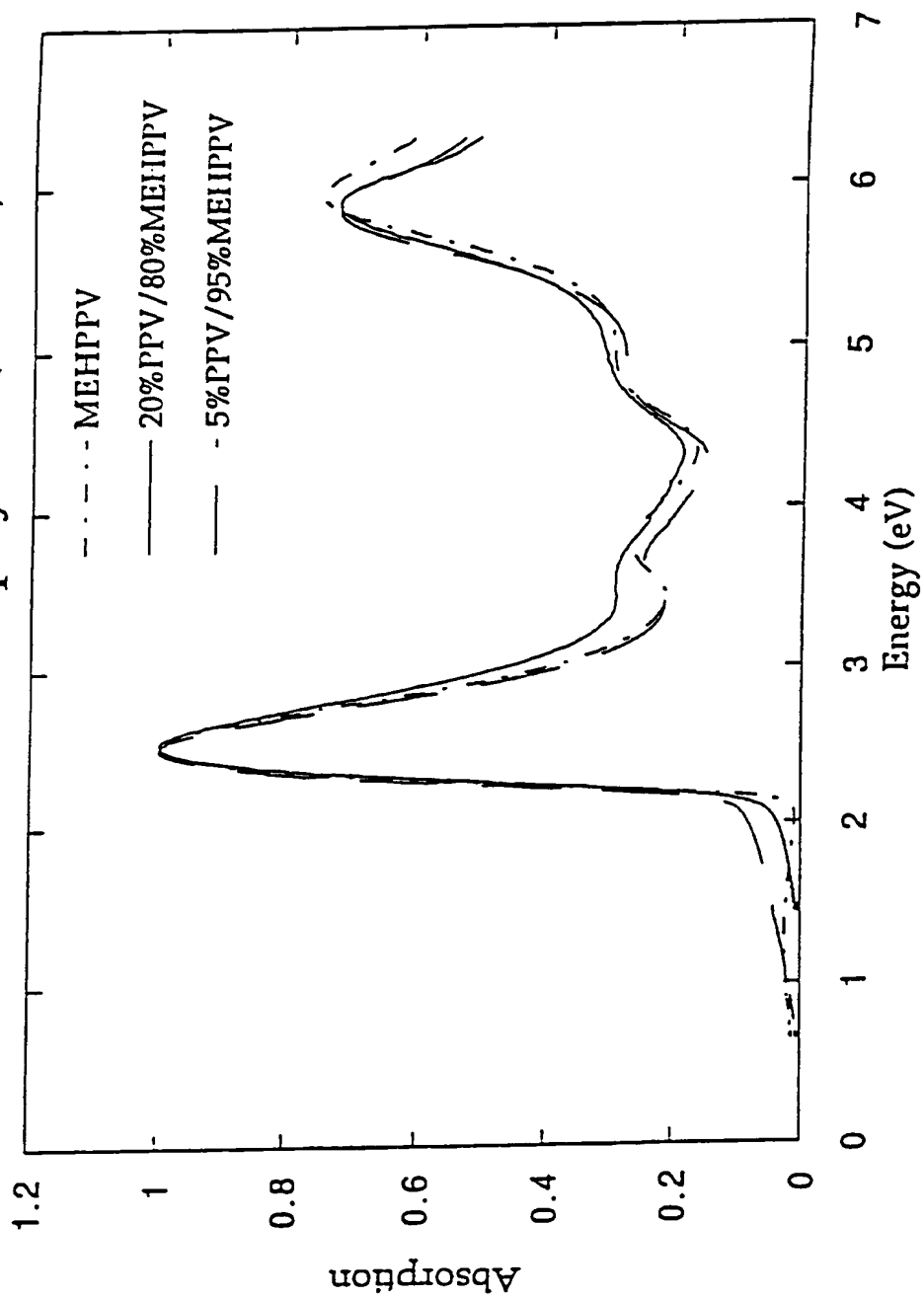


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FIG. 26

MEH-PPV / PPV copolymers (soluble)

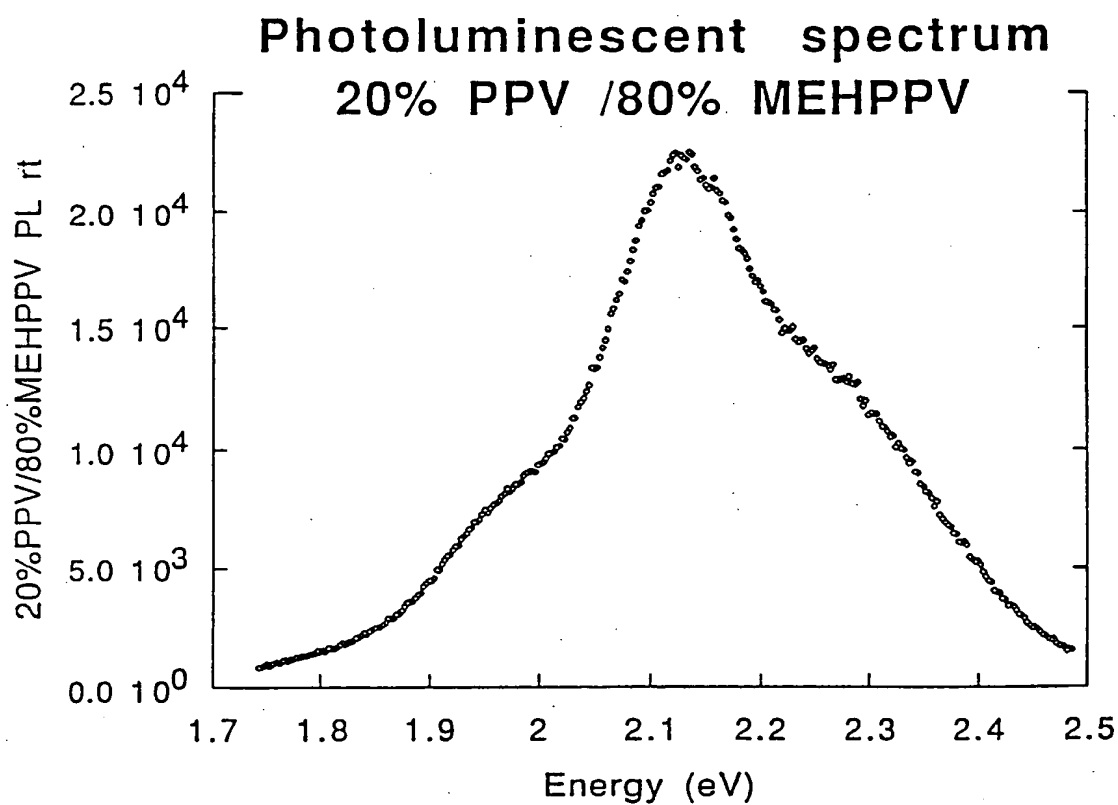




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FIG. 27a

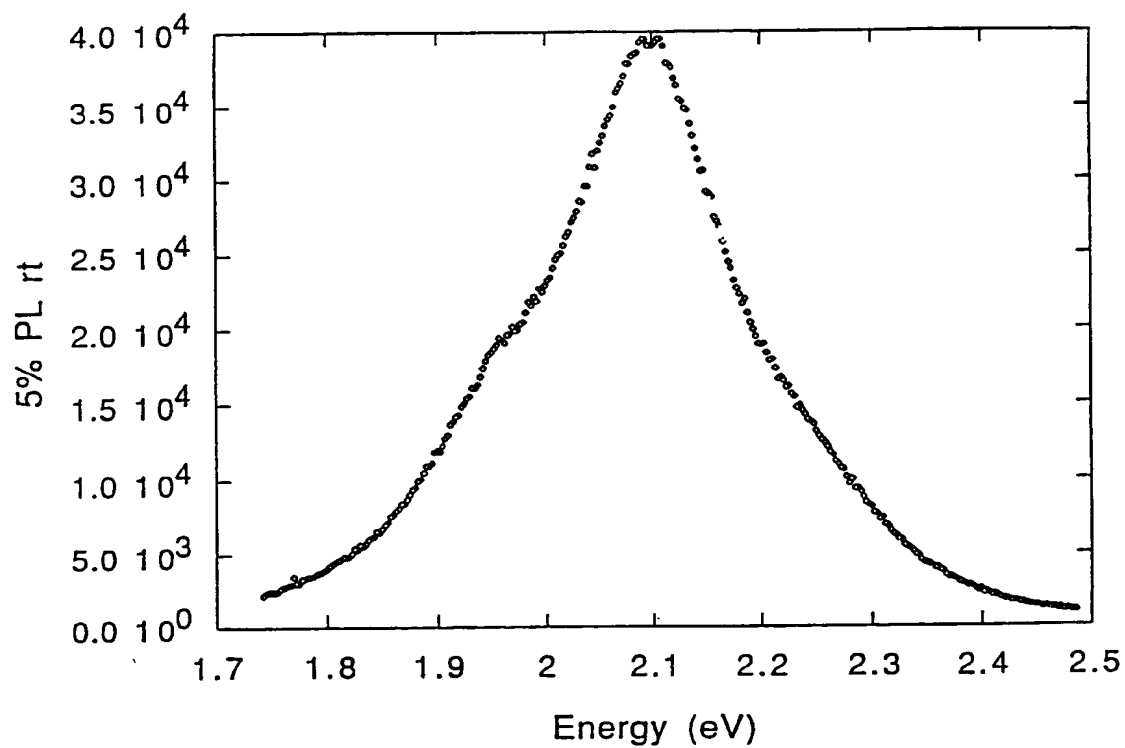
• 20%PPV/80%MEHPPV PL rt



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*FIG. 27b*

**Photoluminescence Spectrum  
5%PPV/95%MEHPPV**

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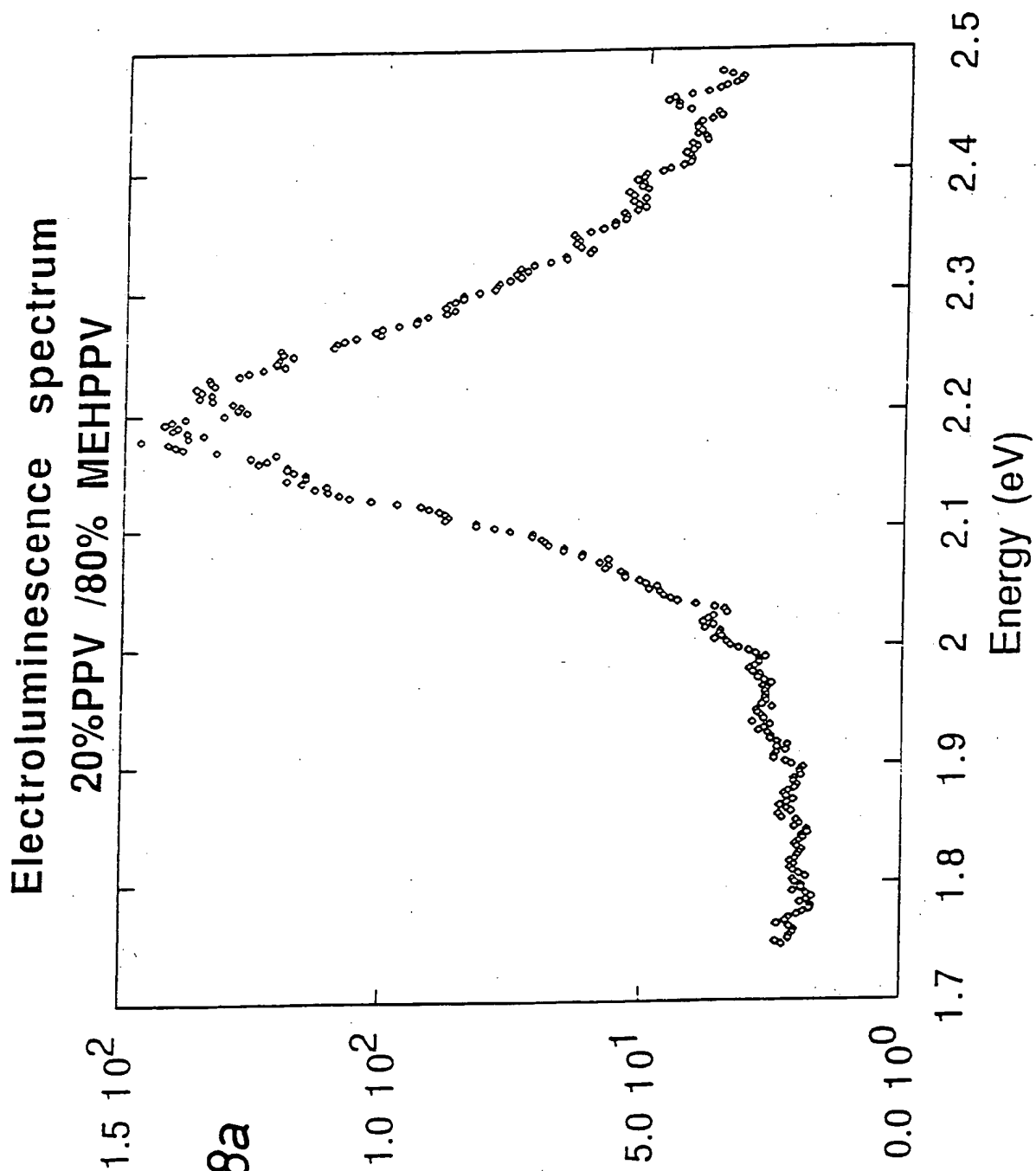
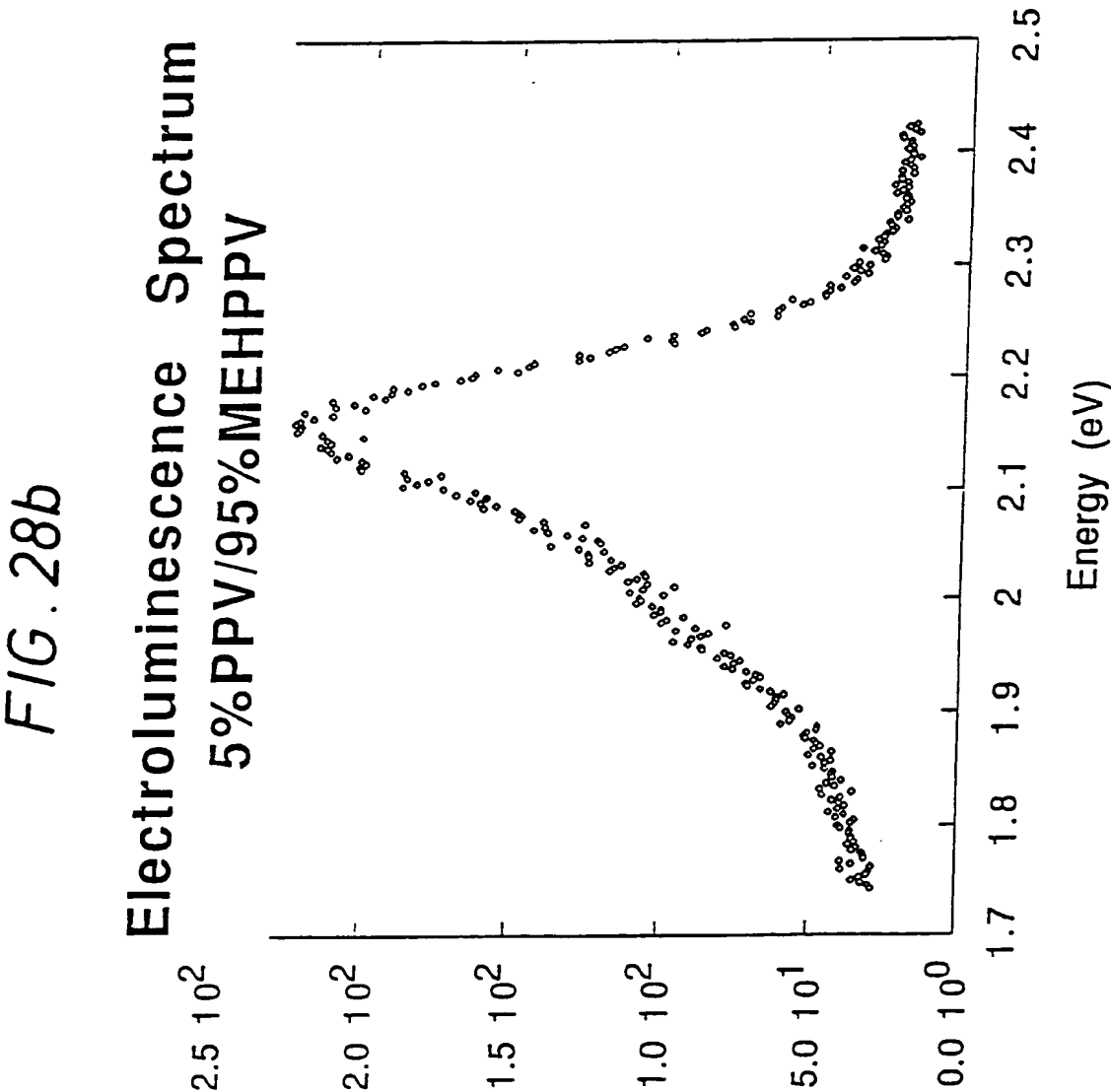


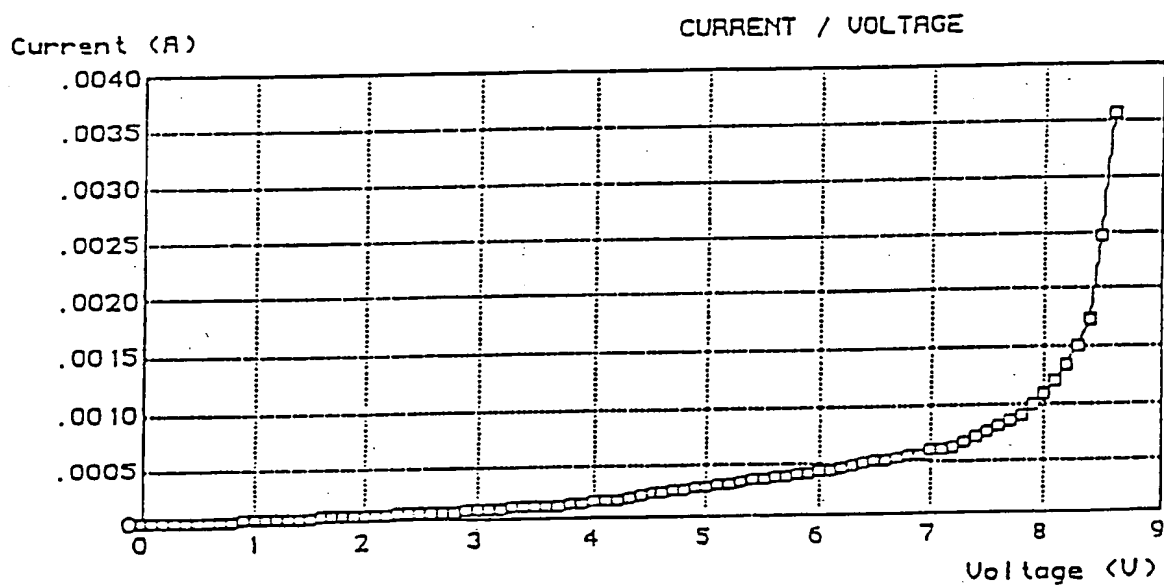
FIG. 28a

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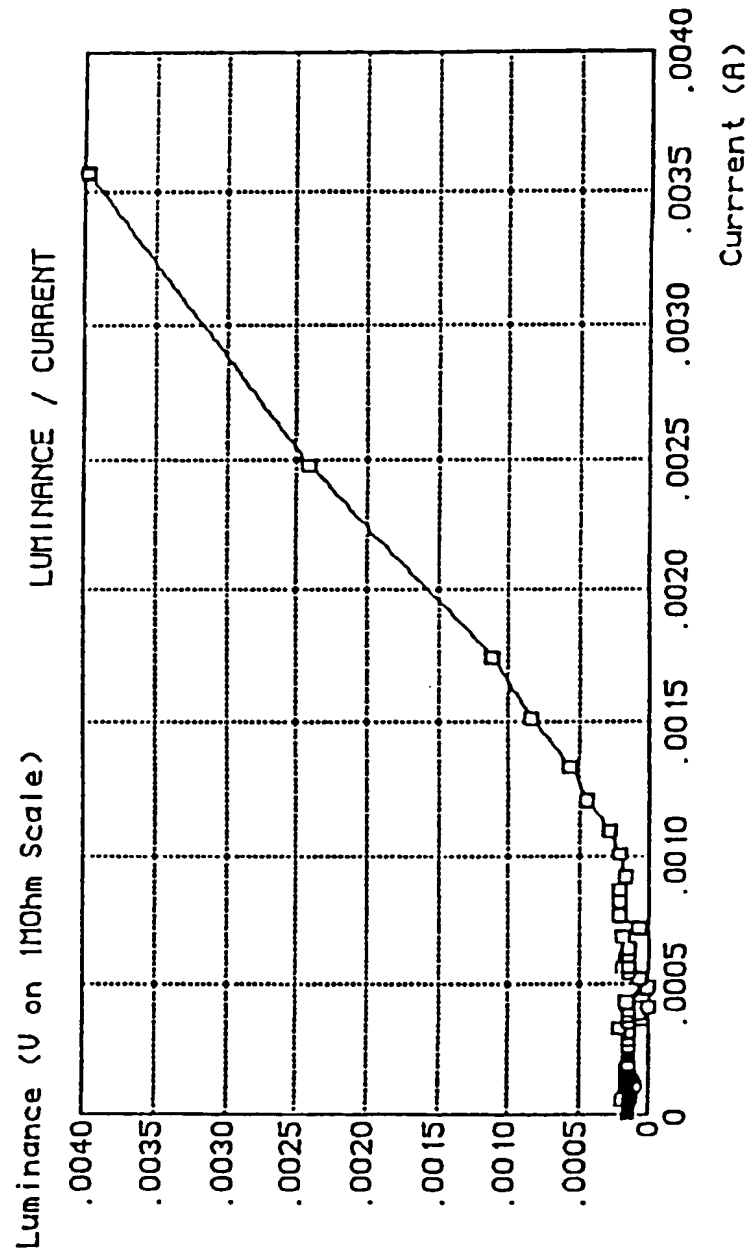
FIG. 29a



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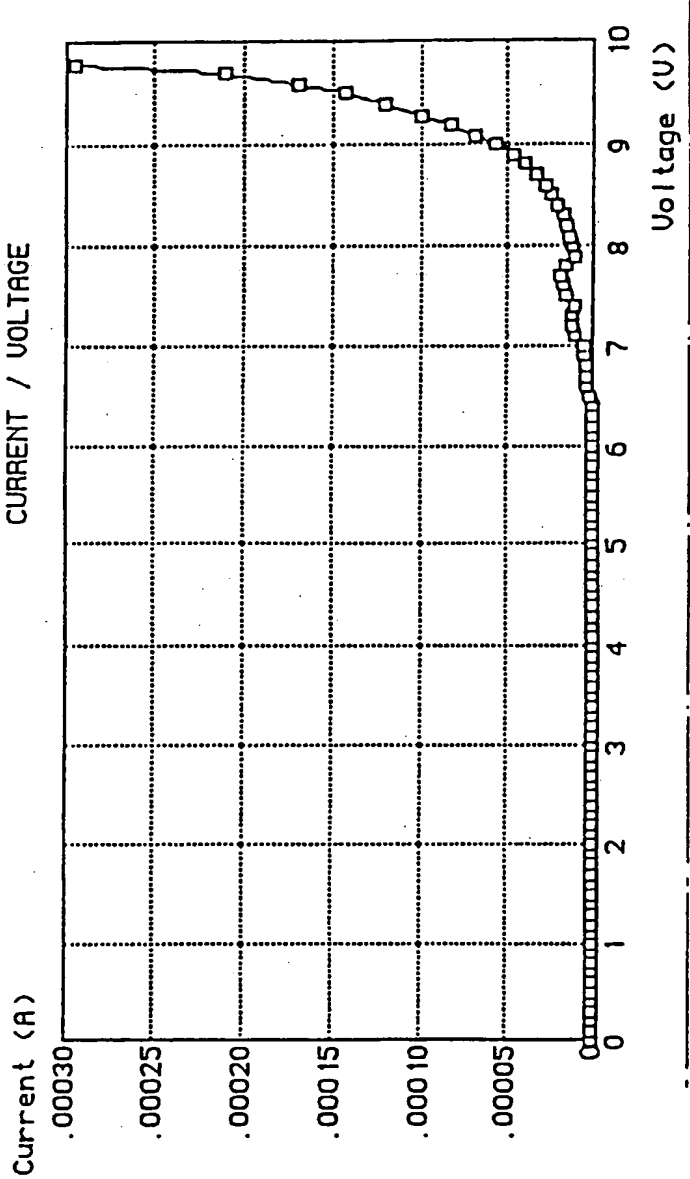
FIG. 29b



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FIG. 30a



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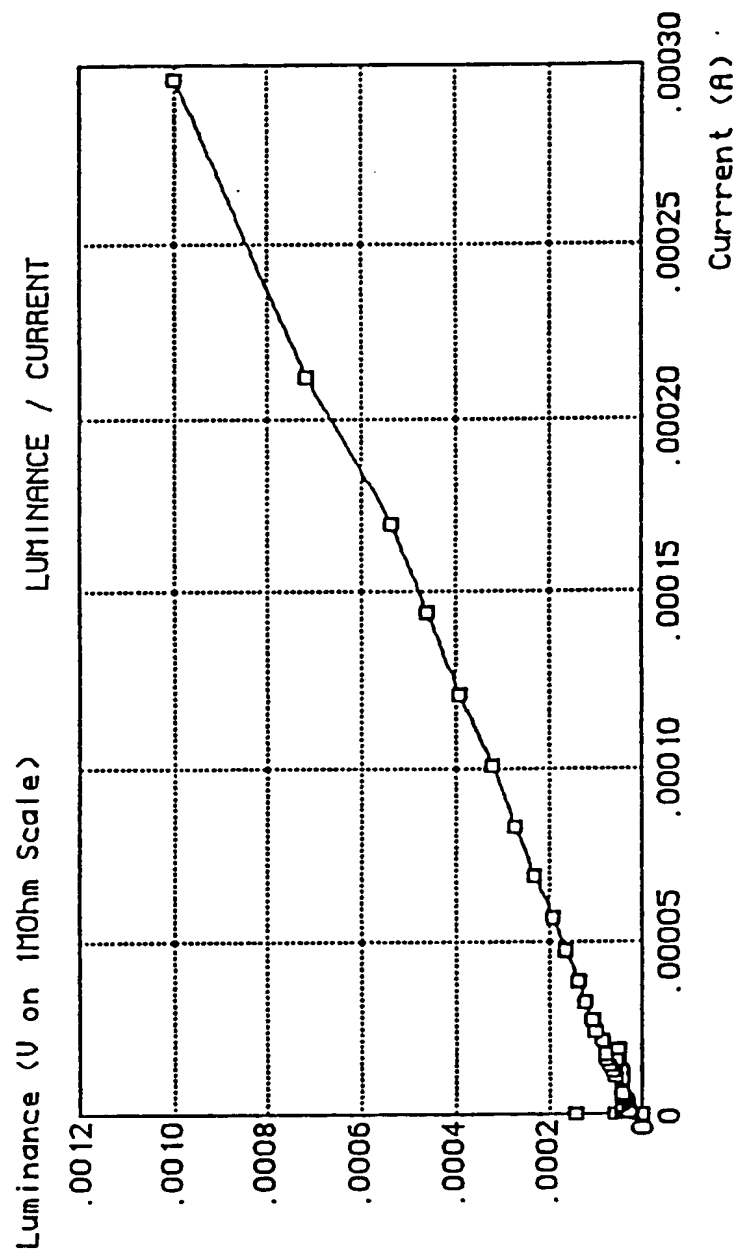
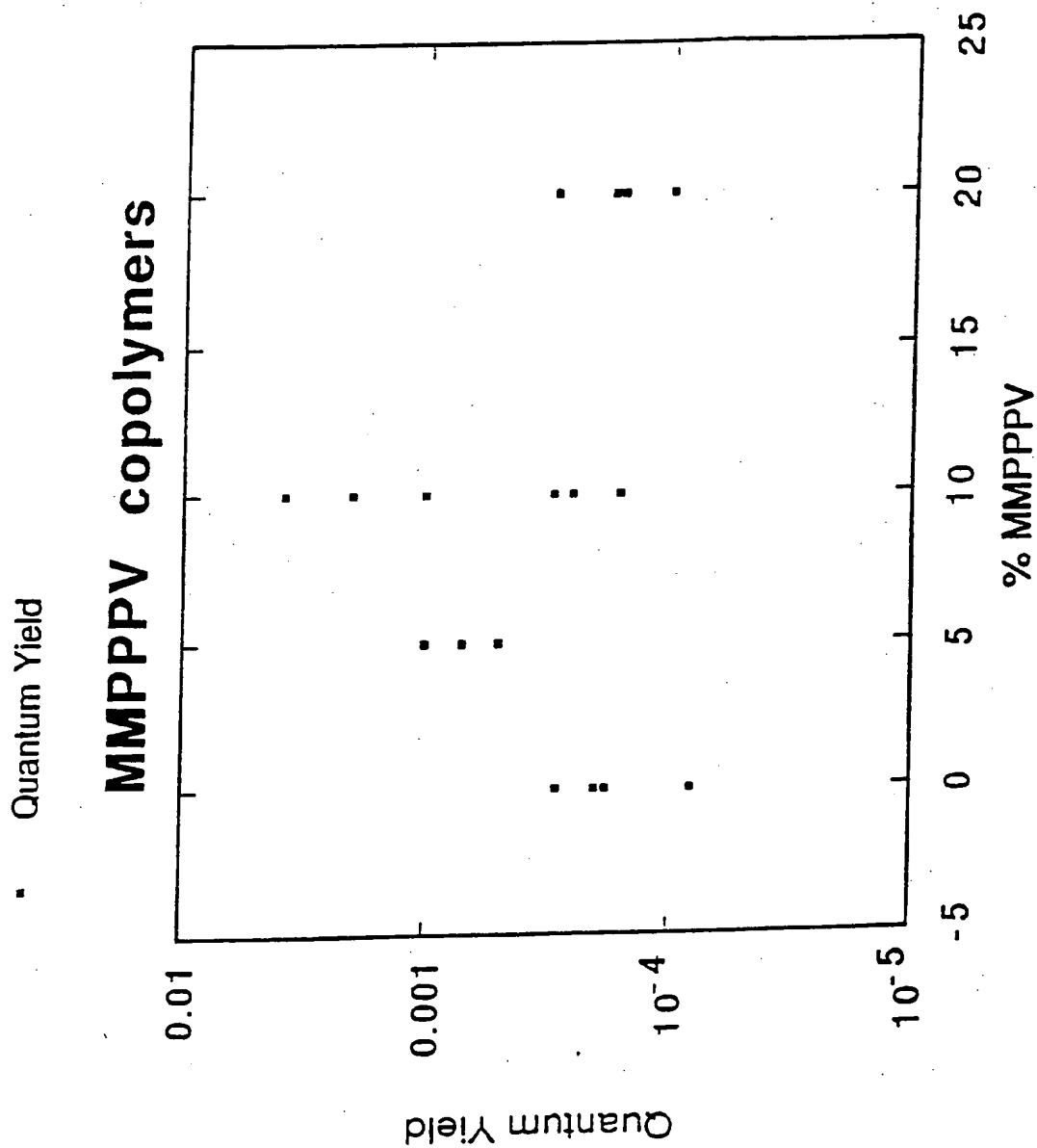


FIG. 30b



FIG. 31



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*FIG. 31a*

Photoluminescence at room temperature  
of MEHPPV, 5% PPV / 95% MEHPPV, 20% PPV / 80% MEHPPV

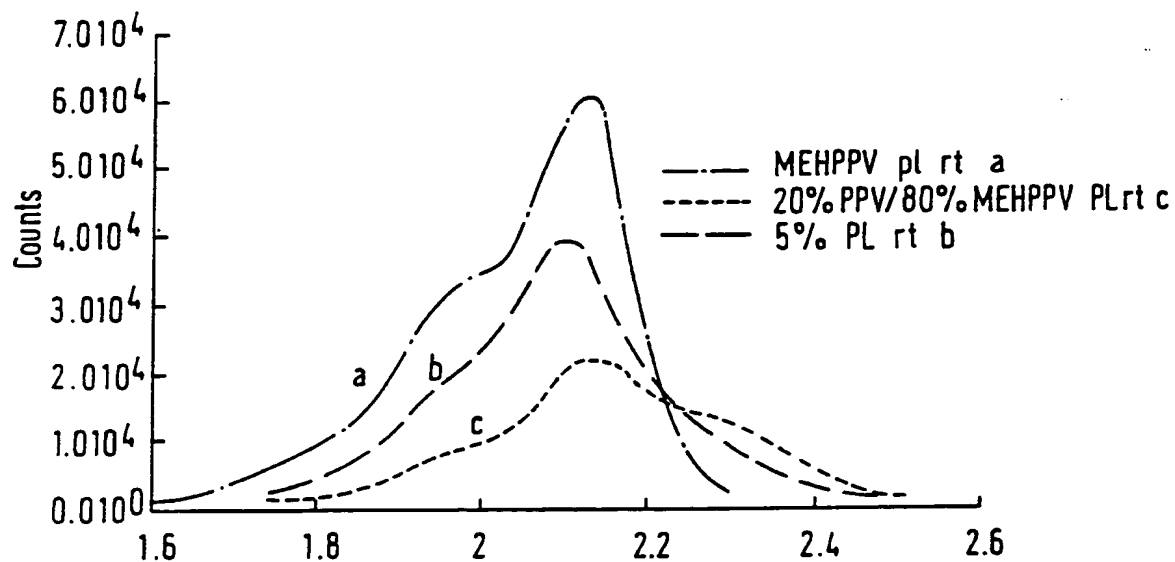
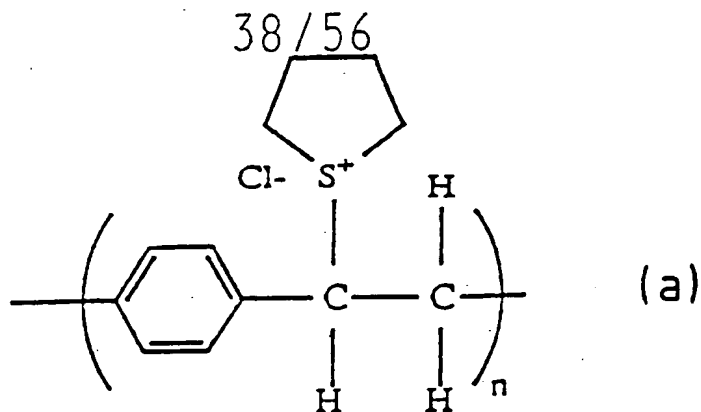
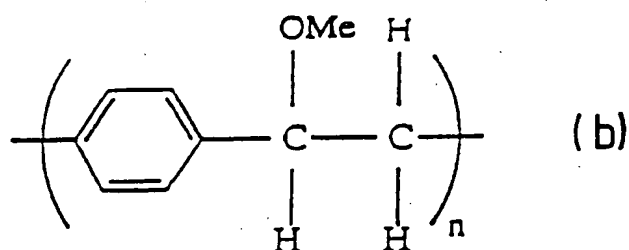


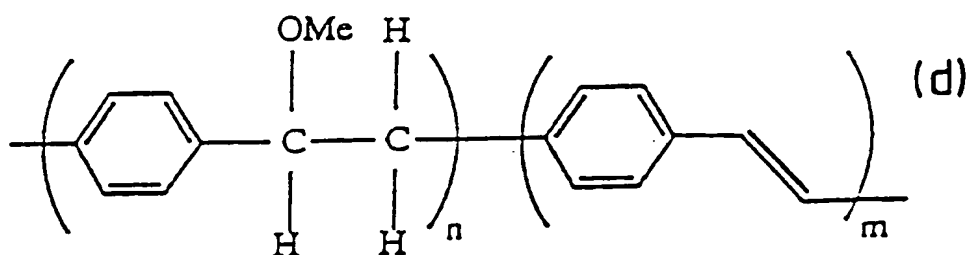
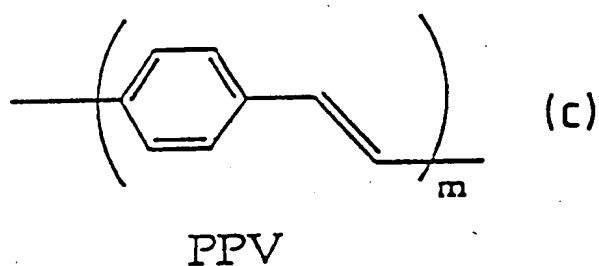
FIG. 32



THT-leaving PPV Precursor



MeO-leaving PPV Precursor



Partially converted MeO-leaving PPV

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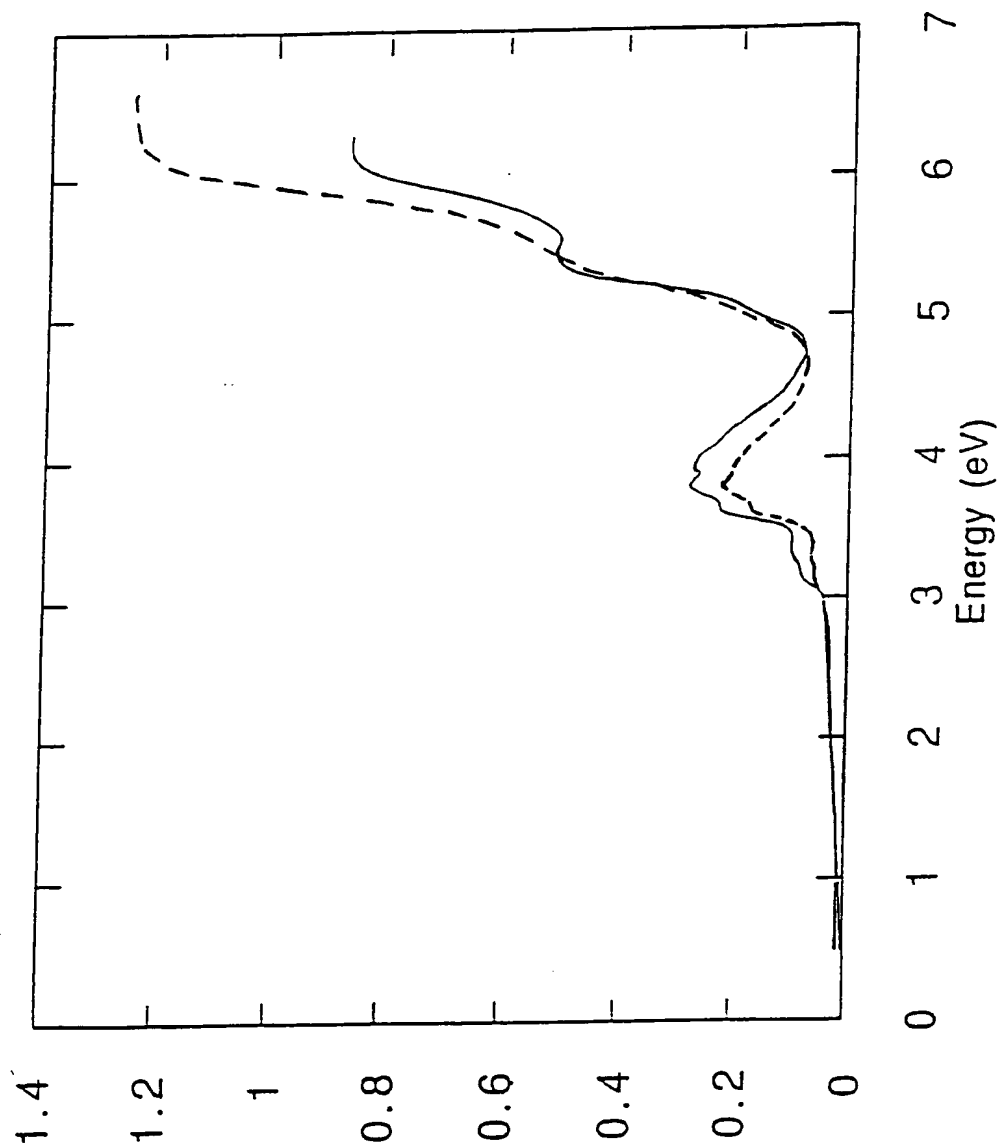
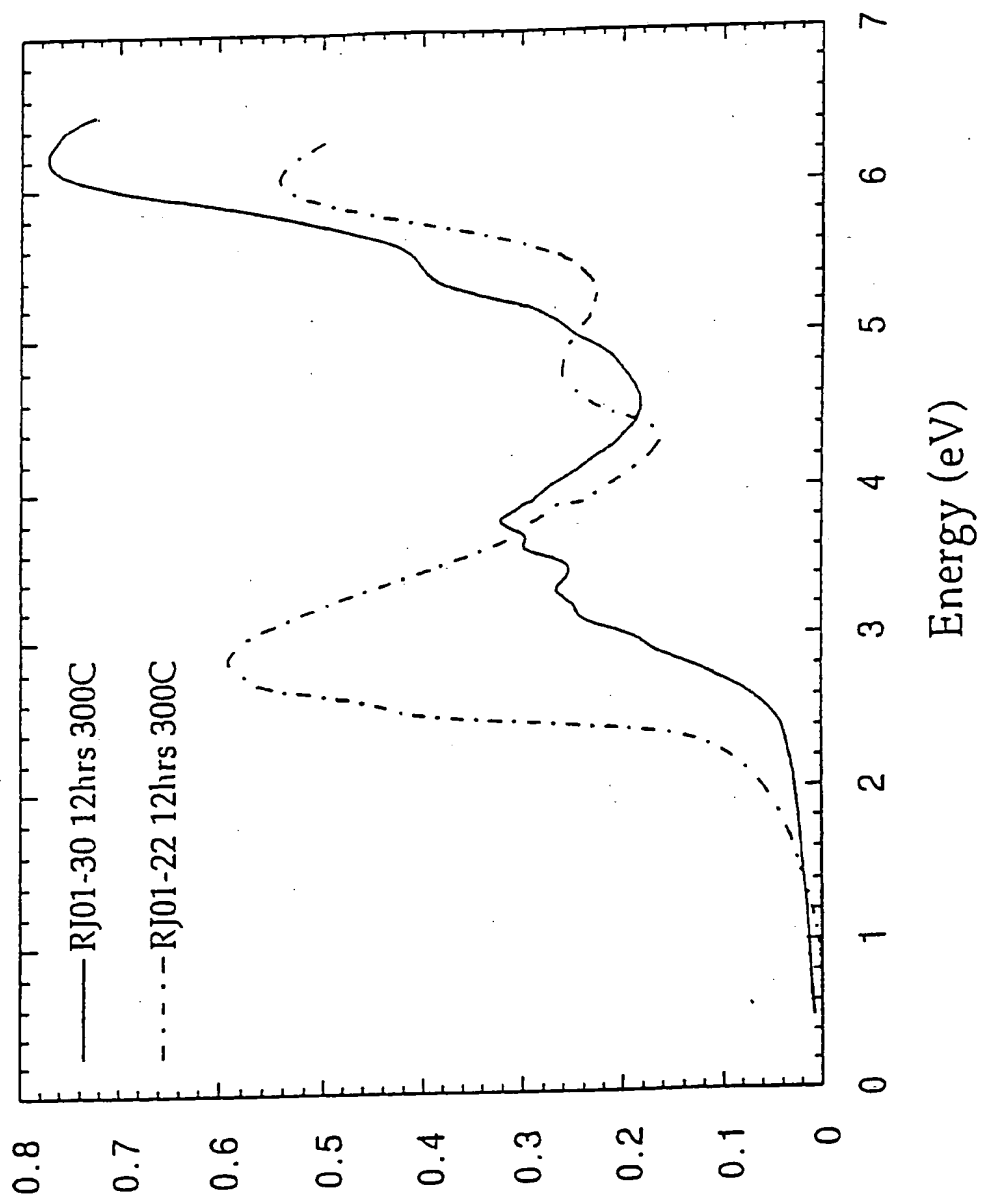


FIG. 33

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FIG. 34



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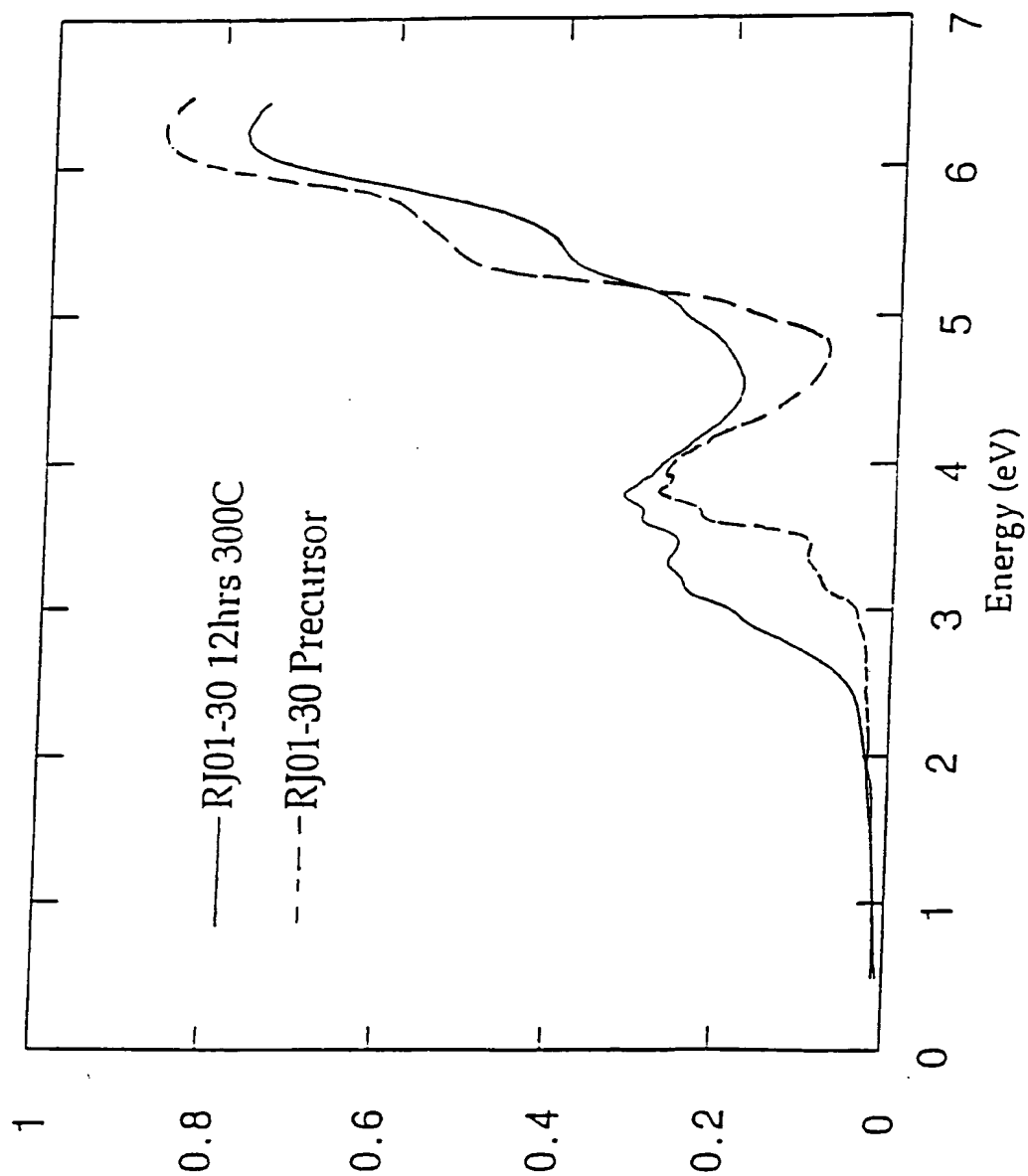
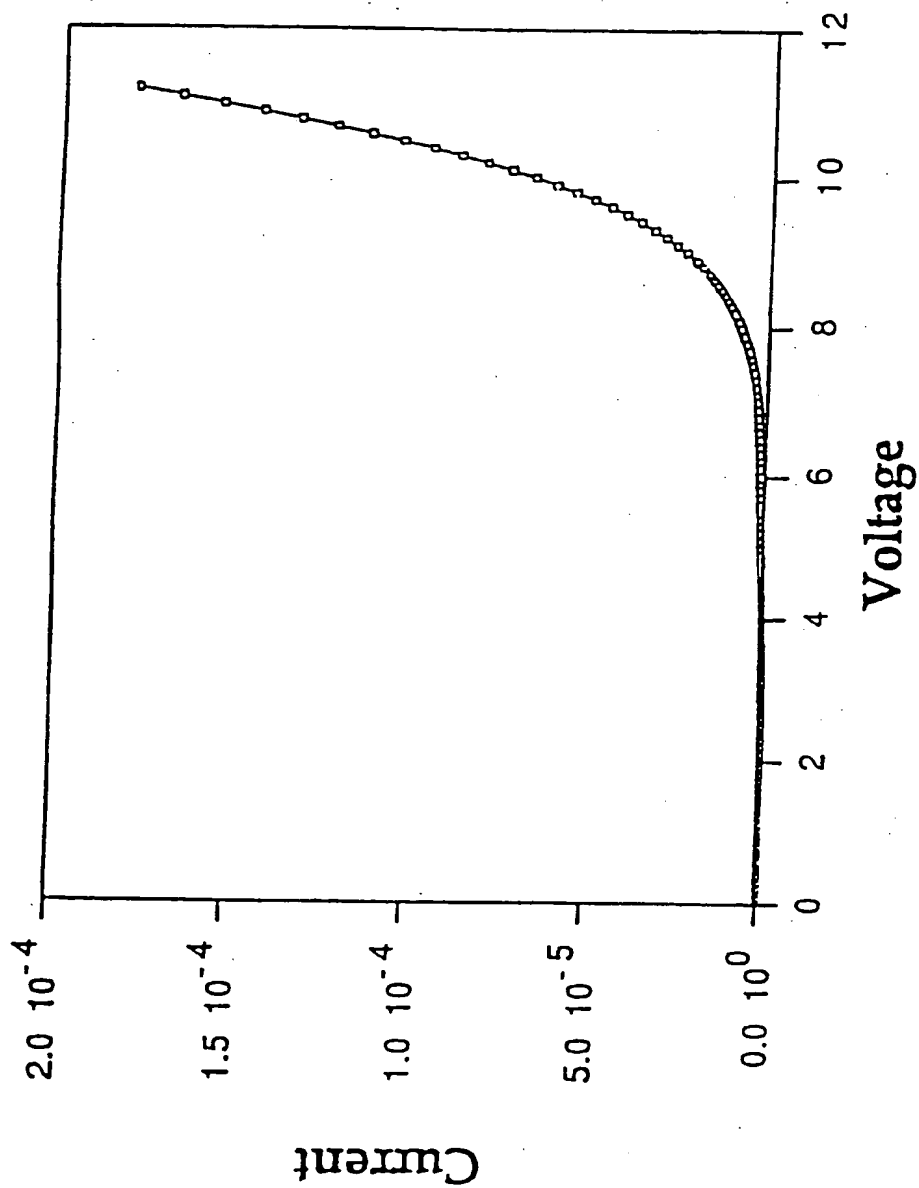


FIG. 35

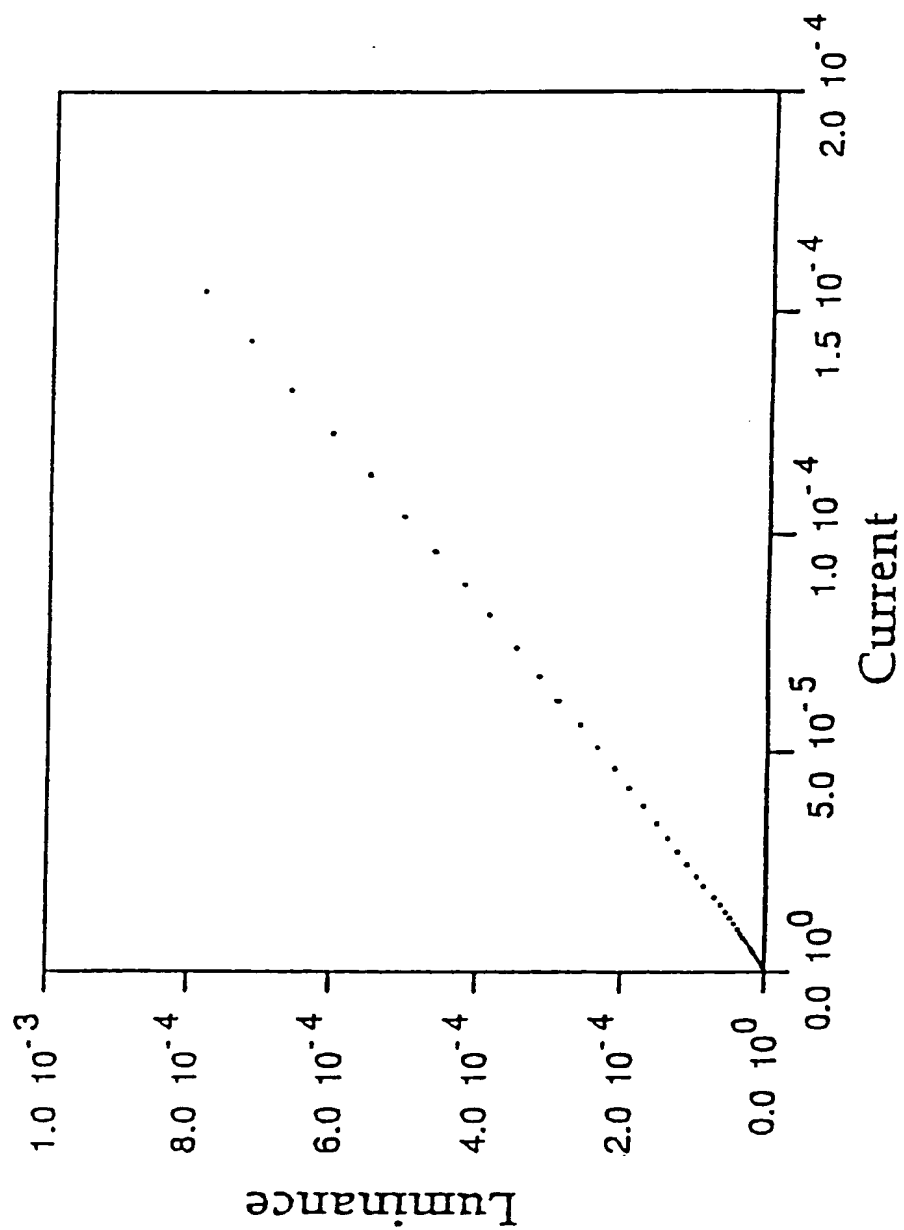
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FIG. 36a



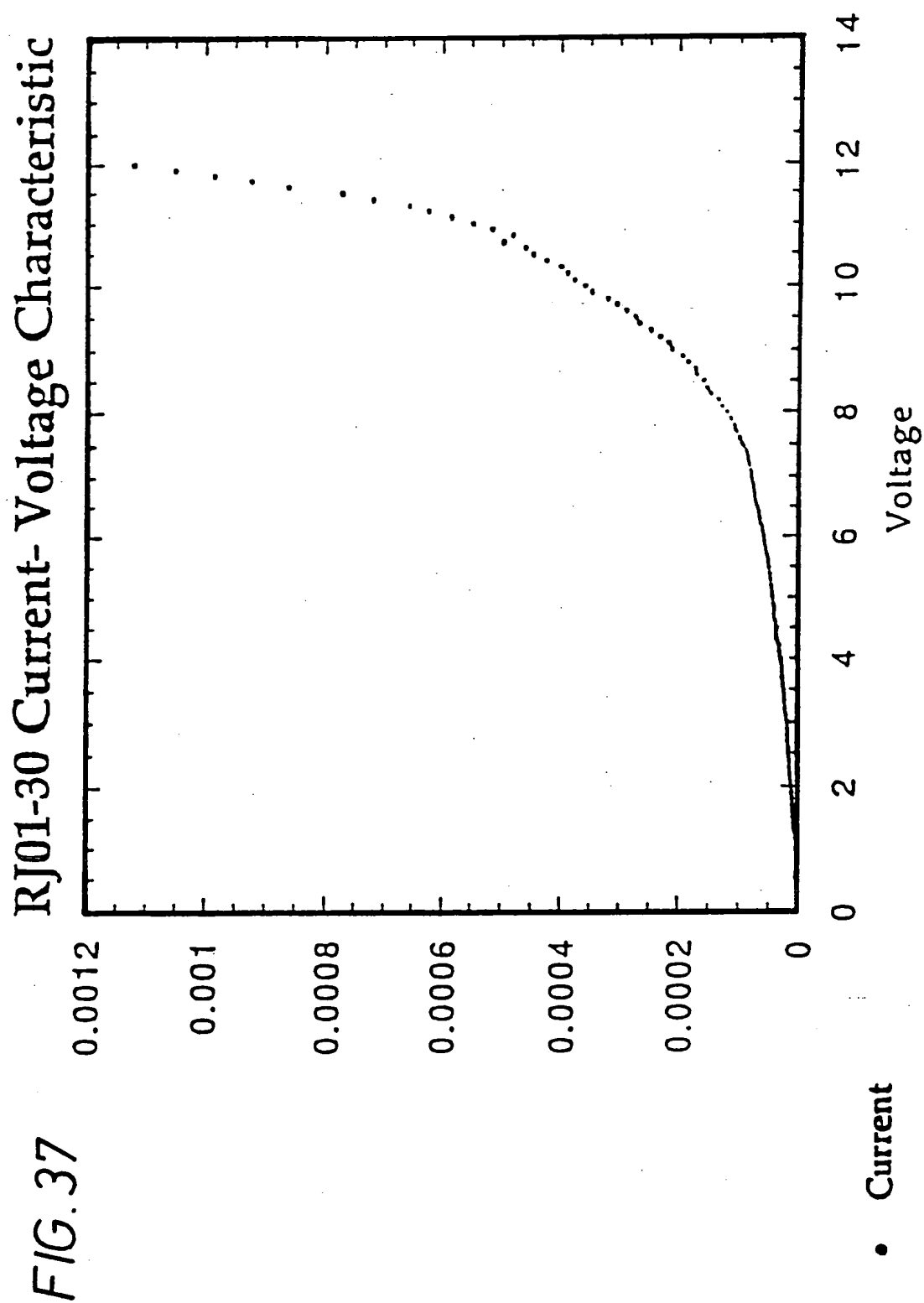
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FIG. 36b

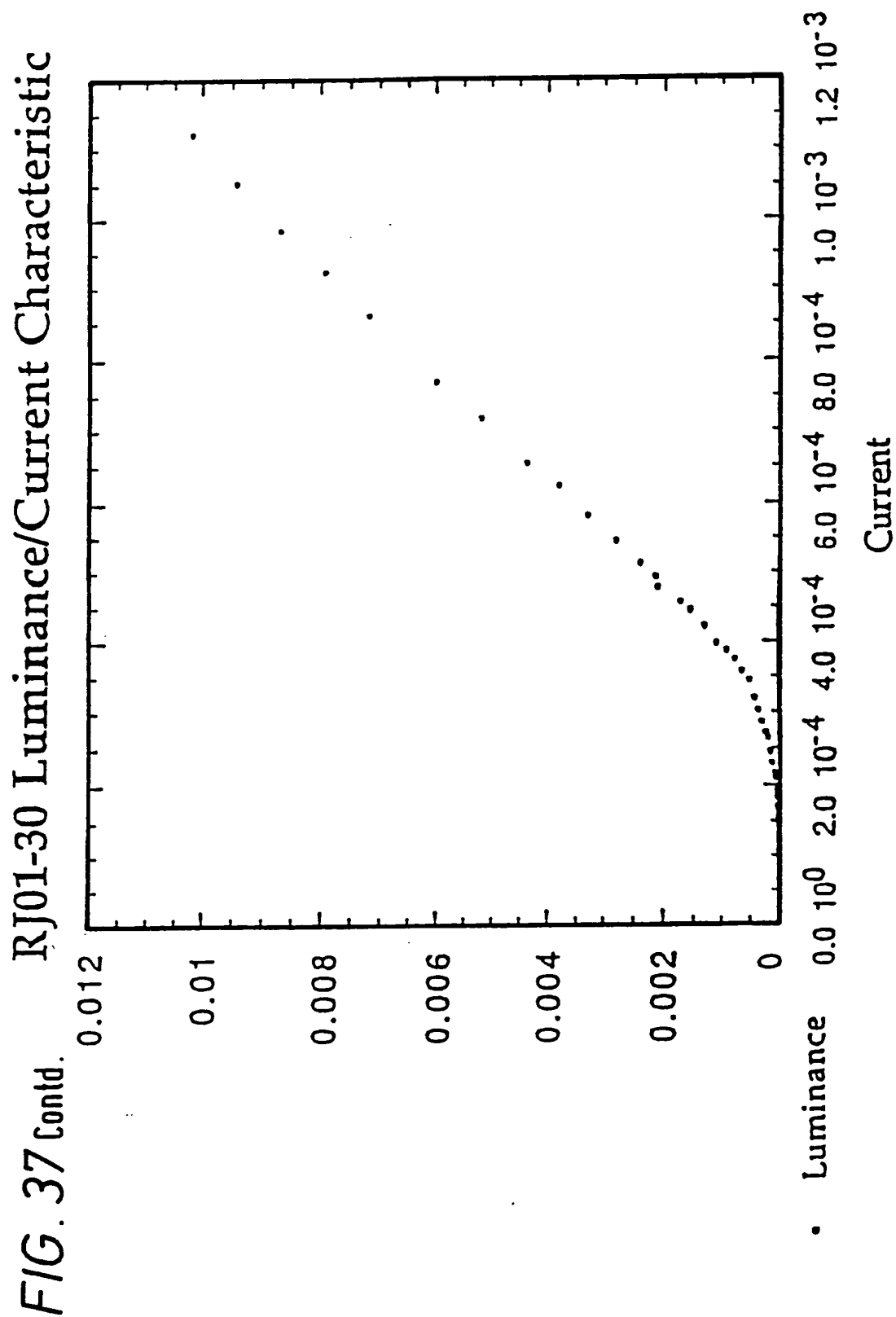




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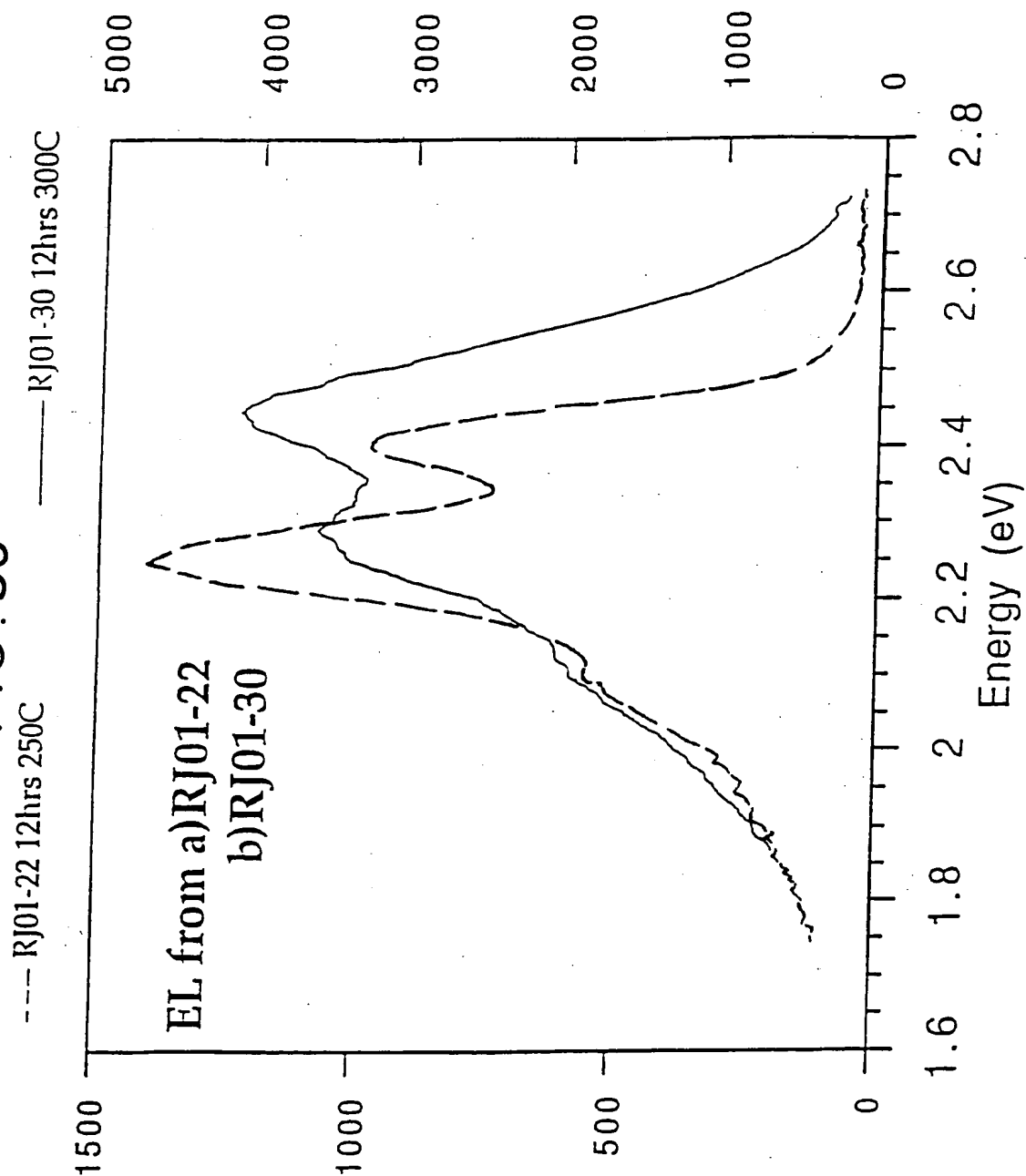


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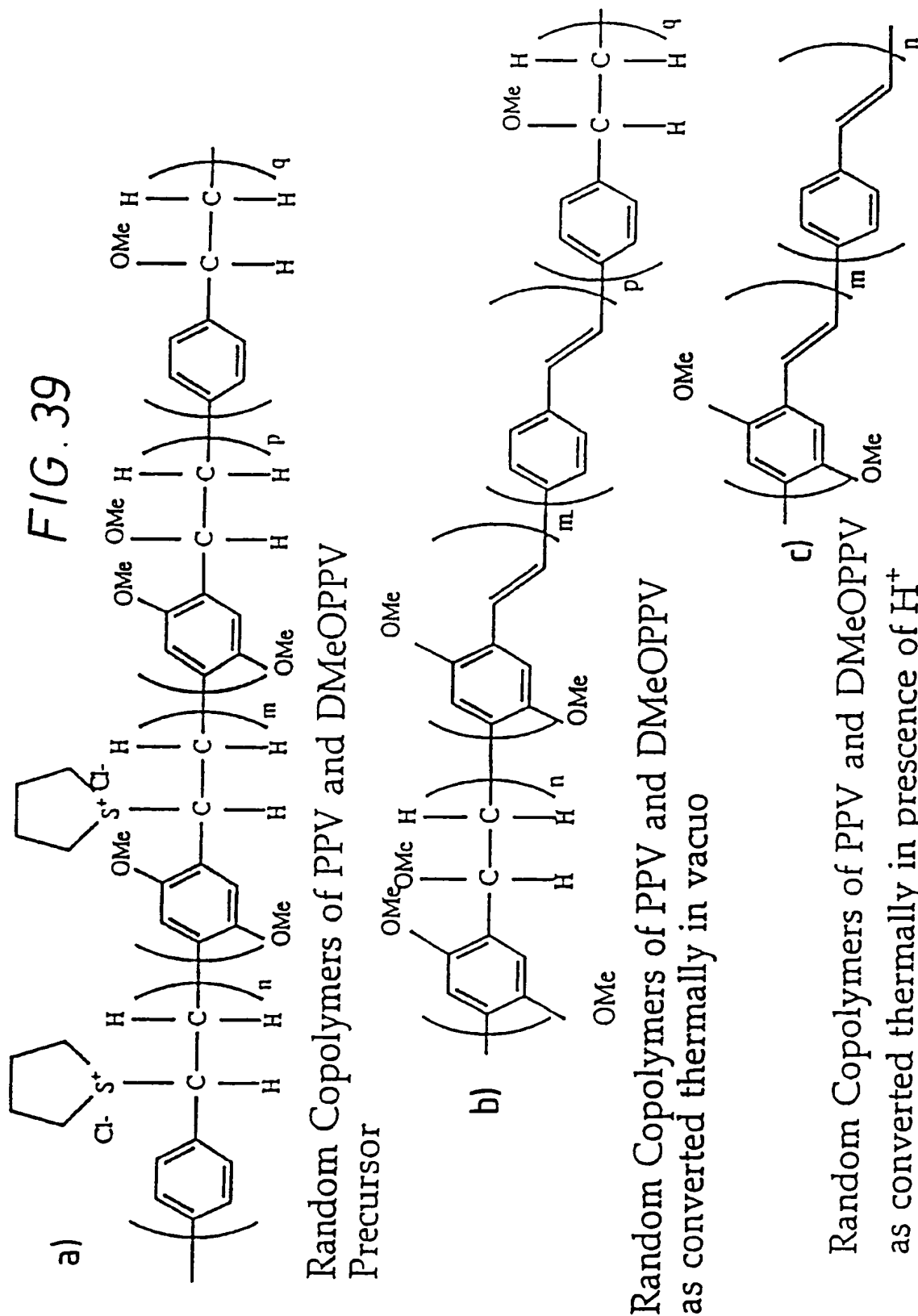


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FIG. 38

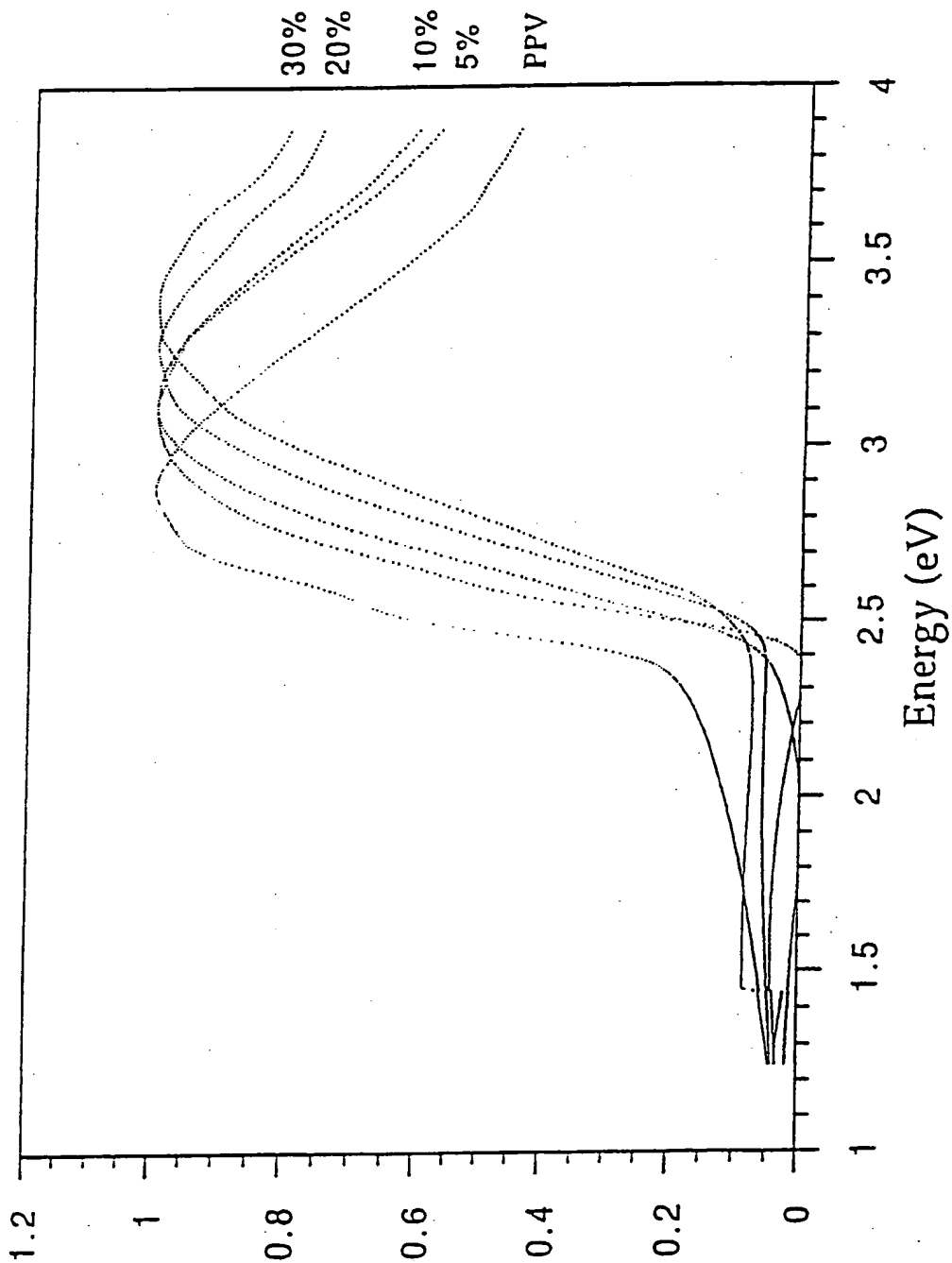


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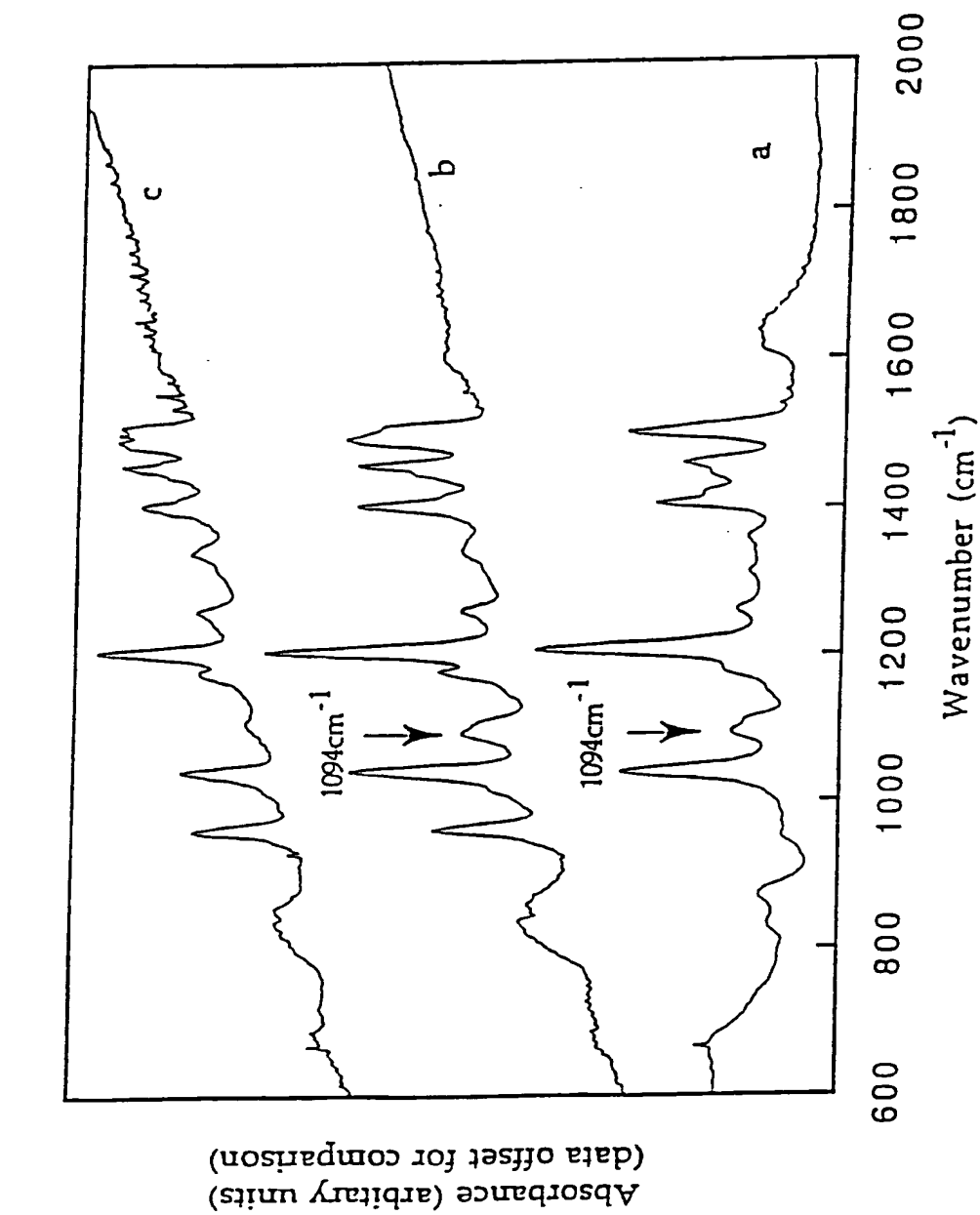


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**FIG. 40** Copolymers of PPV and DMeOPPV  
converted for 2 hours at 220C



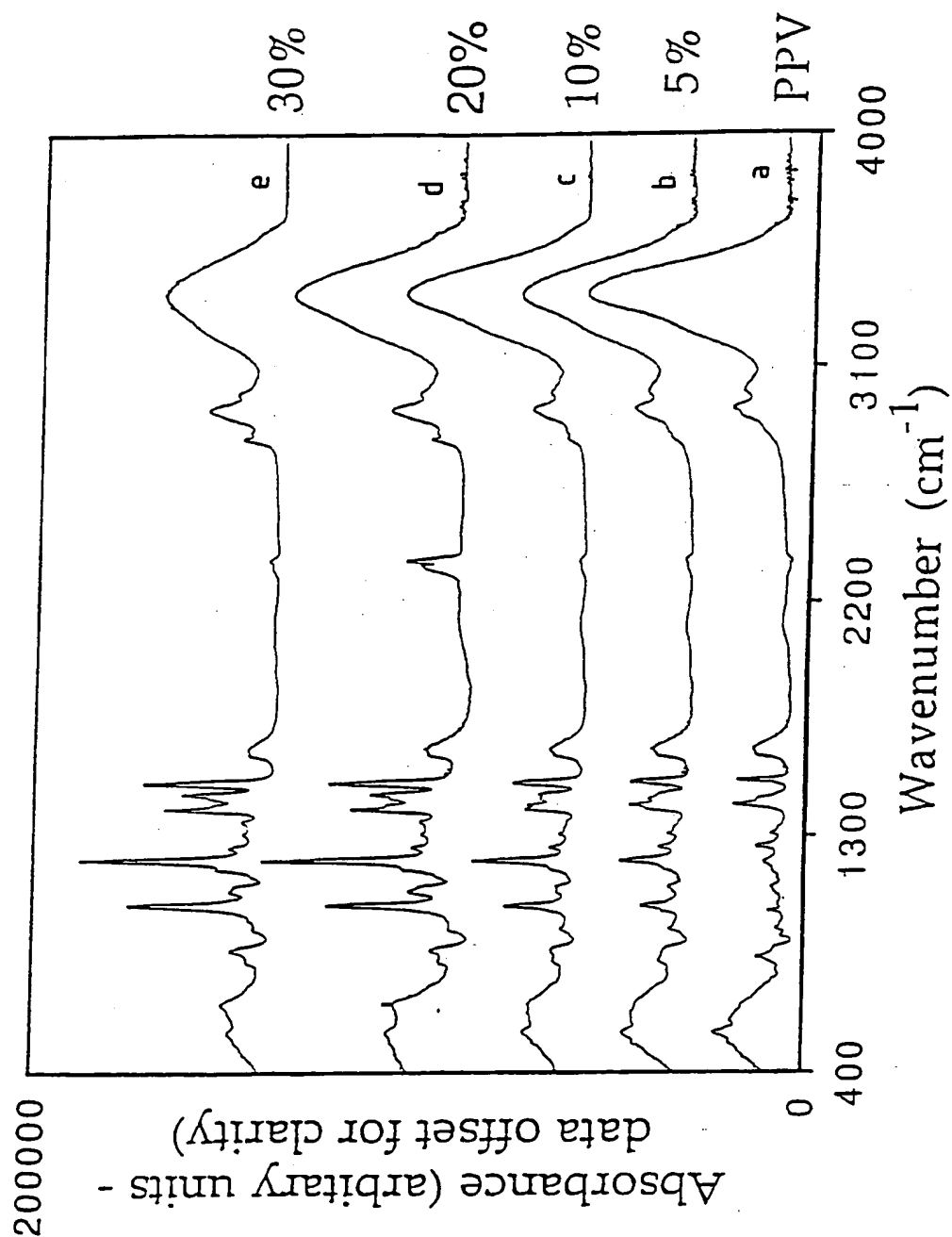
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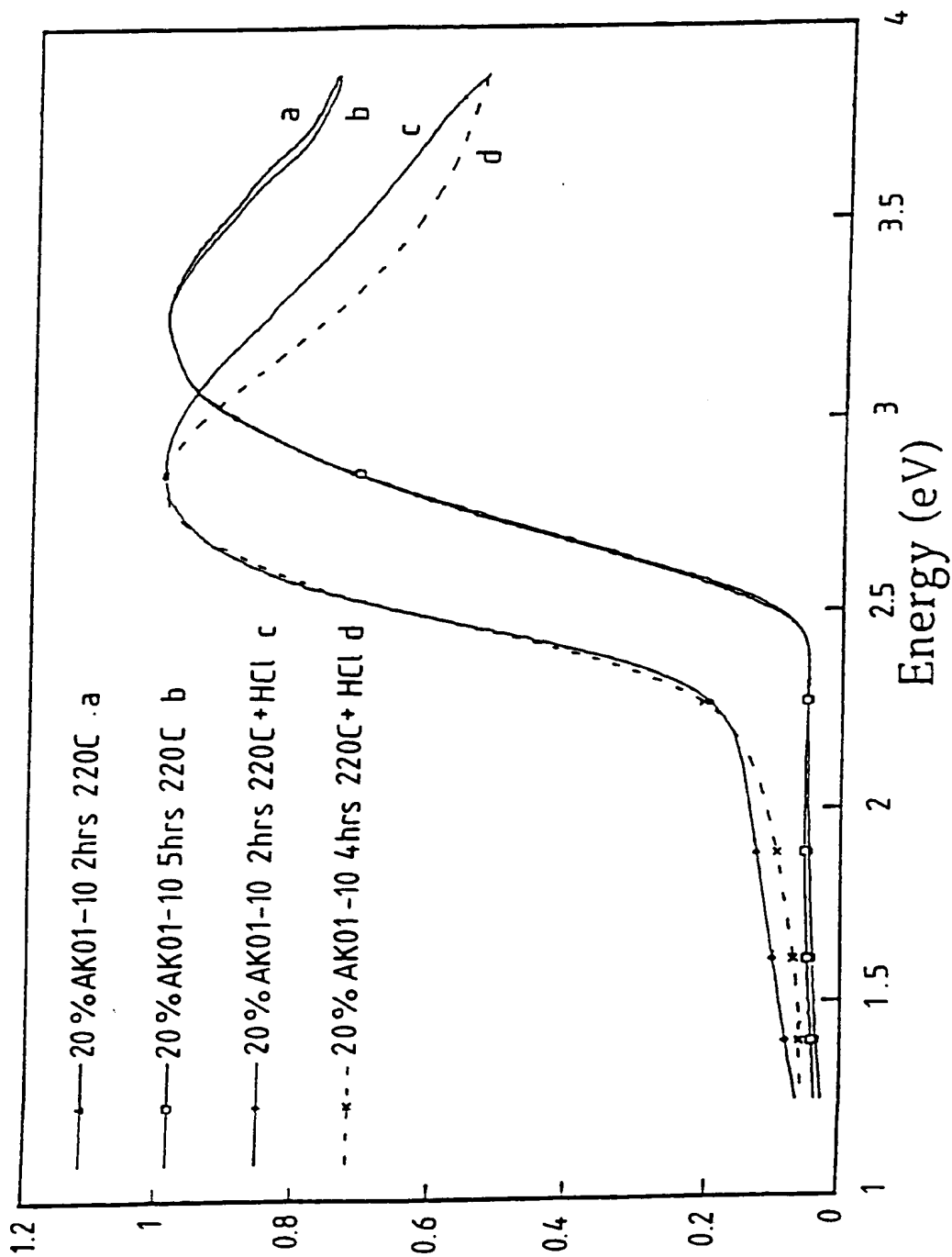
Precursors of Random Copolymers of  
Dimethoxy-PPV and PPV

FIG. 42



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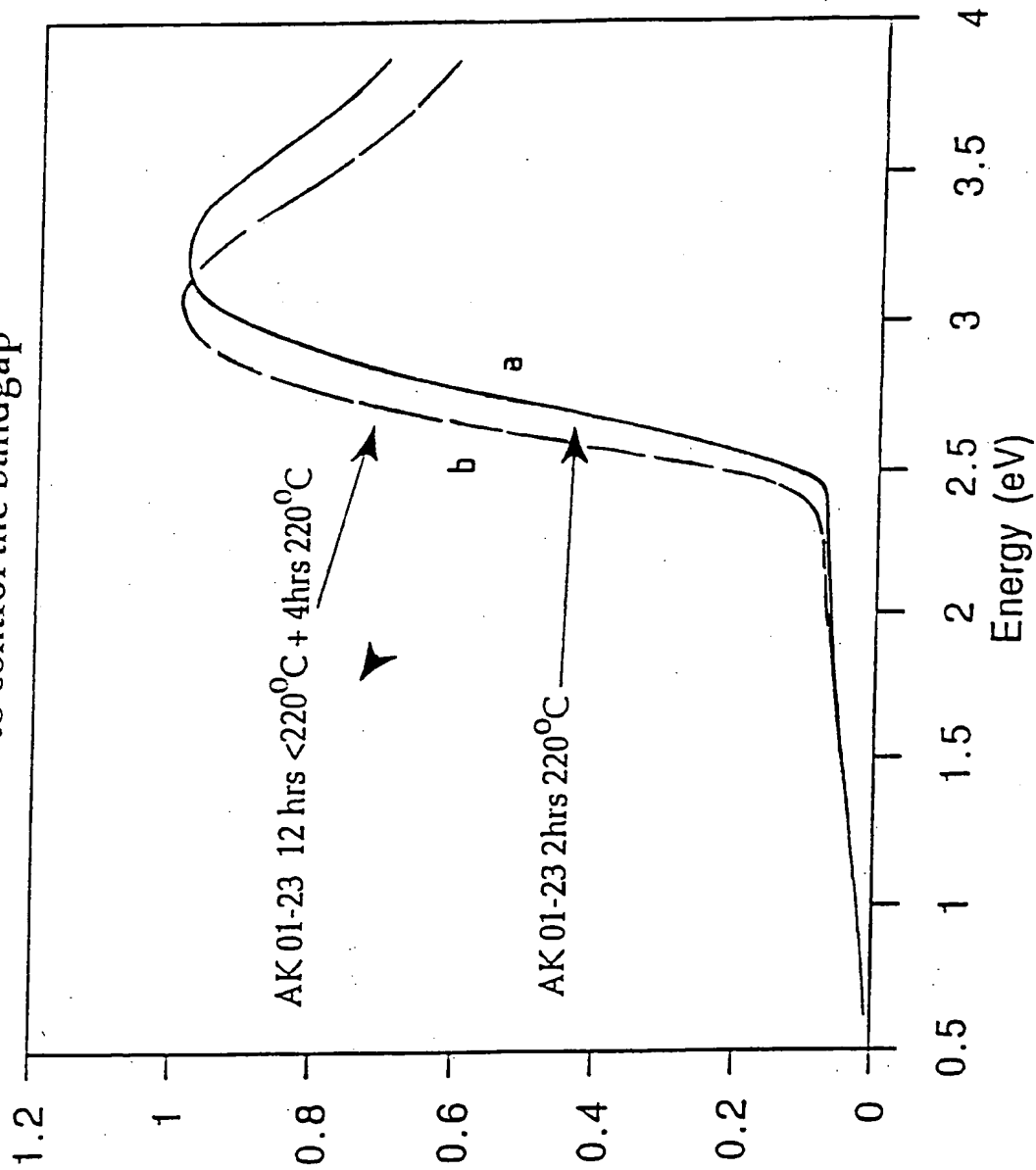
FIG. 43





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15% Copolymer converted under different conditions  
to control the bandgap



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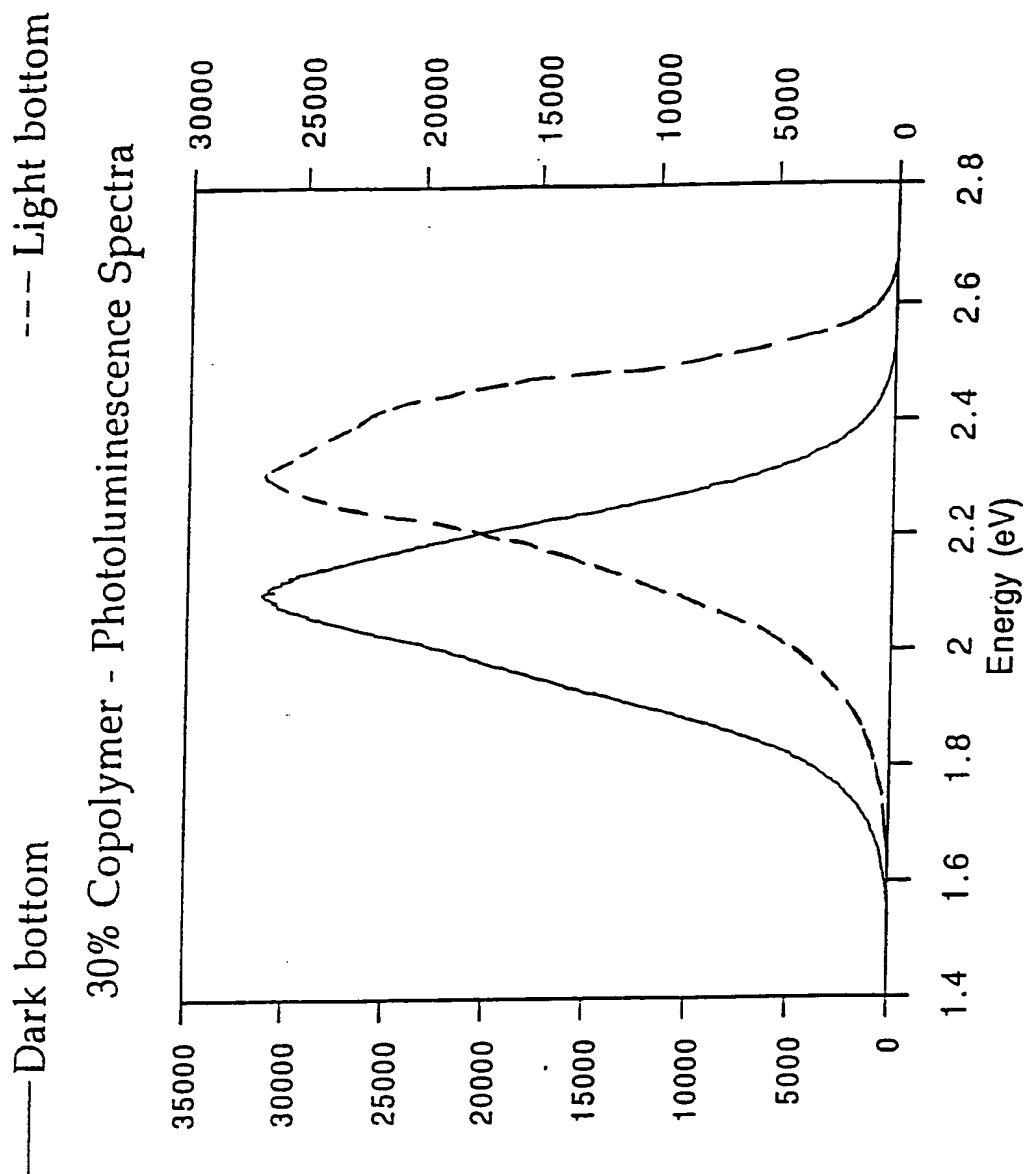


FIG. 45

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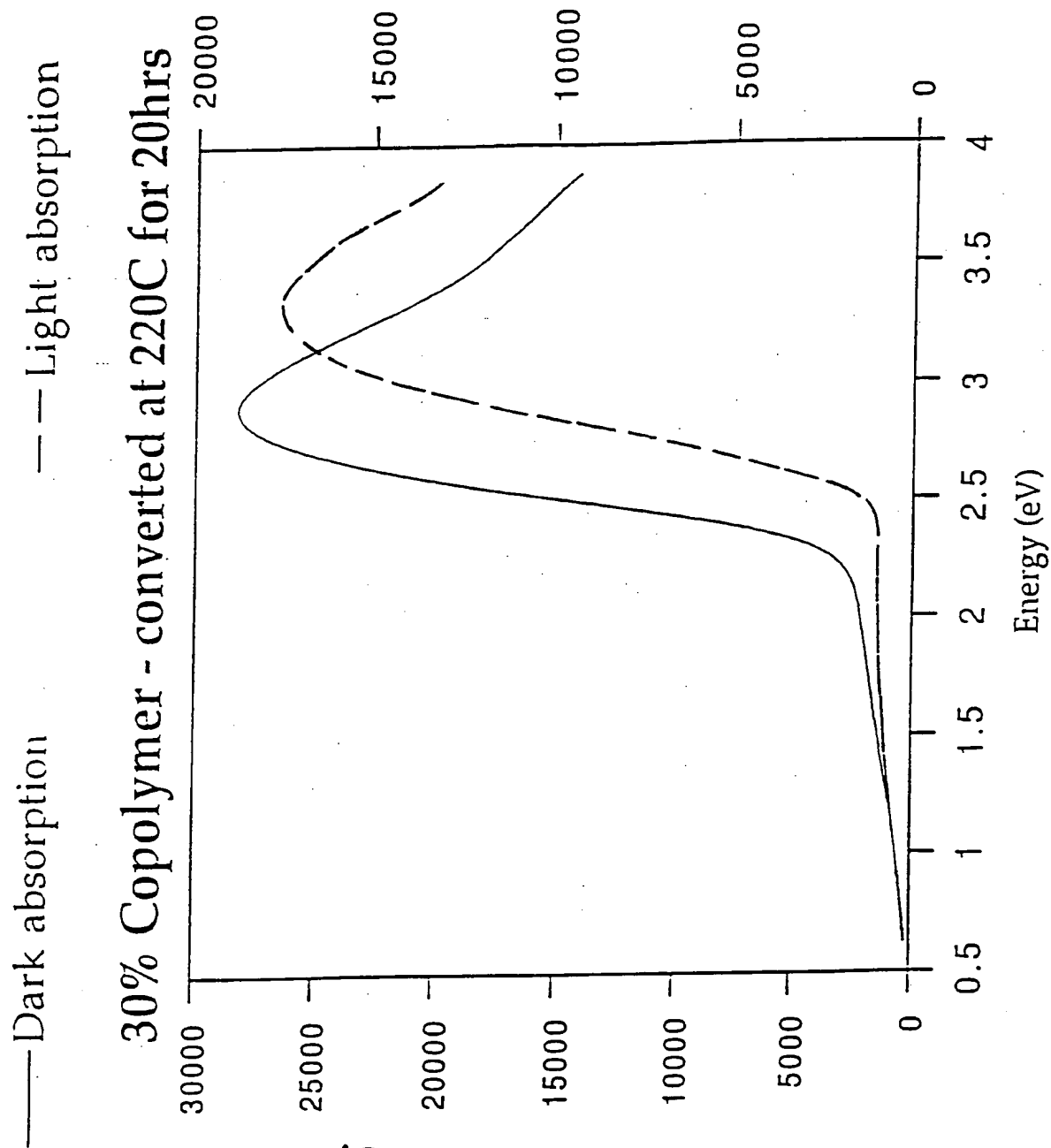


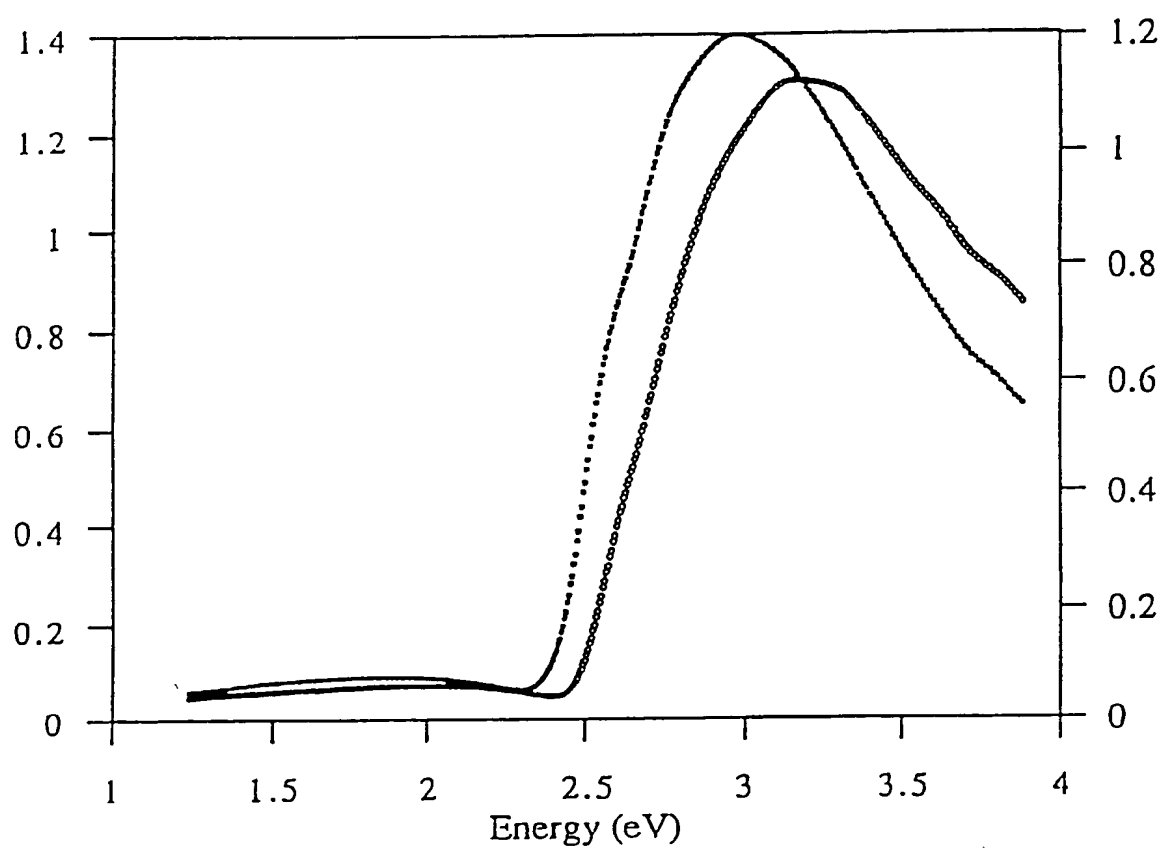
FIG. 46

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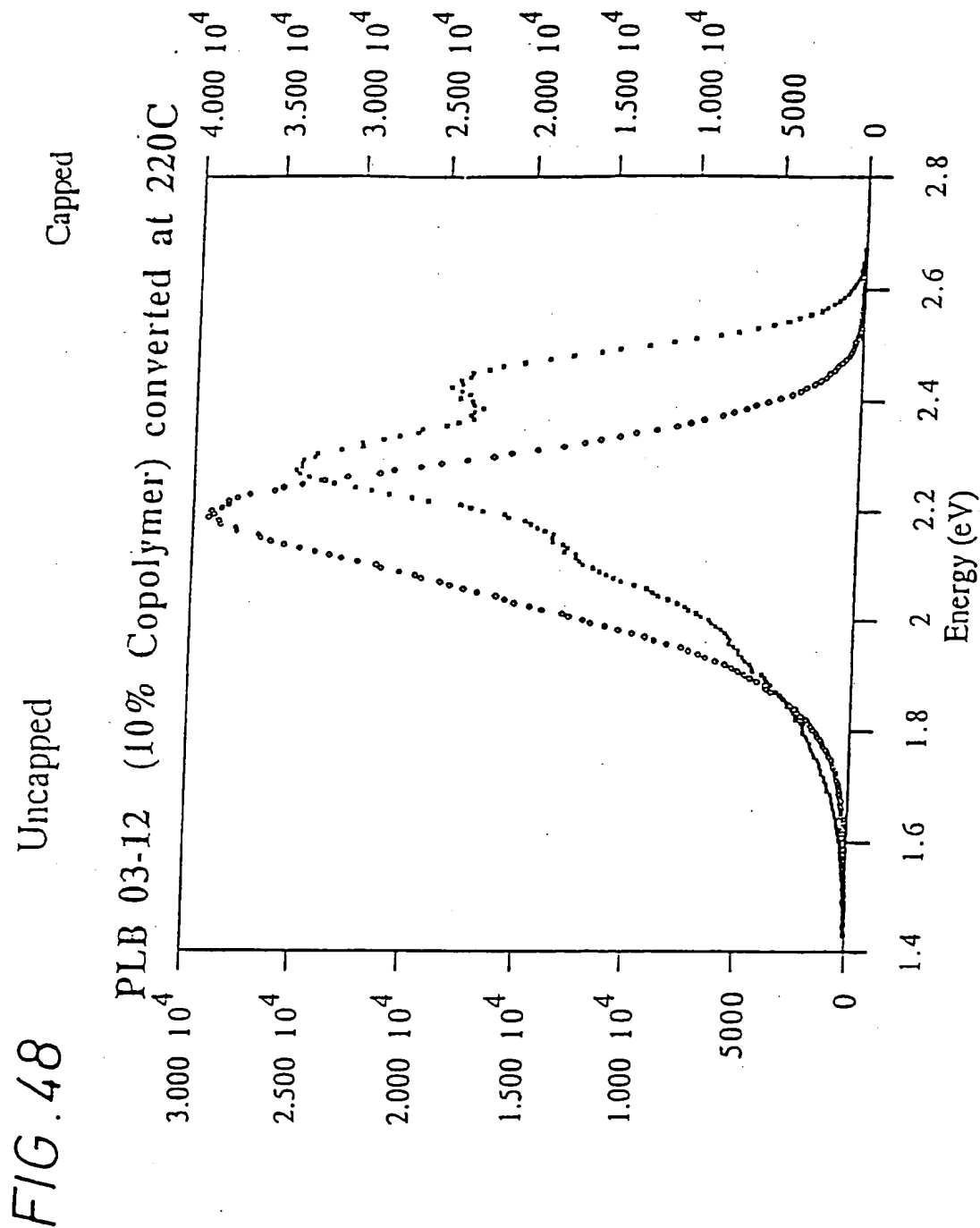
*FIG. 47*

Capped

Uncapped



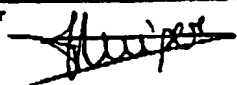
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## INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 91/01420

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (If several classification symbols apply, indicate all) <sup>6</sup>		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int.C1.5 H 05 B 33/14	C 08 G 61/02 C 08 G 61/12	H 01 B 1/12
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched <sup>7</sup>		
Classification System	Classification Symbols	
Int.C1.5	C 08 G	H 01 B H 05 B
Documentation Searched other than Minimum Documentation to the Extent that such Documents are included in the Fields Searched <sup>8</sup>		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>9</sup></b>		
Category <sup>10</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
A	POLYMER BULLETIN, vol. 21, no. 4, April 1989, (Heidelberg, DE), H.-K. SHIM et al.: "Electrical conductivity of polyblends of poly(1,4-phenylene vinylene) and poly(2,5-dimethoxy-1,4-phenylene vinylene)", pages 409-413 ---	
A	US,A,4900782 (C.-C. HAN et al.) 13 February 1990 ---	
A	JOURNAL OF MOLECULAR ELECTRONICS, vol. 4, no. 1, January 1988, (Chichester, GB), R.H. FRIEND: "Optical investigations of conjugated polymers", pages 37-46 (cited in the application) --- -/-	
<p><sup>10</sup> Special categories of cited documents: <sup>10</sup></p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"A" document member of the same patent family</p>		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
15-11-1991	13 JAN 1992	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	Mme N. KUIPER 	

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category <sup>a</sup>	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	CHEMISTRY LETTERS, no. 7, 1988, (Tokyo, JP), T. MOMII et al.: "Synthesis of poly(2,5-dimethoxy-p-phenylenevinylene) film through a new precursor polymer", pages 1201-1204 (cited in the application) ---	
A	DE,A,3704411 (DIRECTOR-GENERAL OF AGENCY OF INDUSTRIAL SCIENCE AND TECHNOLOGY, TOKIO) 20 August 1987 ---	
A	EP,A,0182548 (THE BRITISH PETROLEUM CO. P.L.C.) 28 May 1986 ---	
A	US,A,3621321 (D.F. WILLIAMS et al.) 16 November 1971 -----	

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